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Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications

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ABSTRACT

Phase change materials (PCM) in the form of slurries have had an increasingly important role as heat transfer fluids and as thermal energy storage media. Although it is a recent technology in the field of thermal energy storage with phase change materials, the volume of literature begins to be significant. This investigation carries out a compilation of information on two latent thermal fluids: PCM emulsions and microencapsulated PCM slurries (mPCM slurries). This review presents tables containing information on the different PCM emulsions and mPCM slurries studied by different researchers, as well as commercially available products. Thermophysical and rheological properties are analyzed, making a special effort to analyze heat transfer phenomena, concluding with the enumeration of application examples available in literature.

Contents

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1. Introduction

There is a clear necessity to rationalize the use of energy in modern society. One of the main contributions to the rational use of energy is thermal energy storage. There is a great technical potential in the use of thermal energy storage substituting the combustion of fossil fuels, allowing for a greater use of energies which do not present constant supply, such as residual heat or renewable energies. Energy sources can be more efficient using short- and long-term storage. Thermal energy storage can also be used to shave or eliminate the peak of electricity demand, including more expensive electricity that is generated during on-peak hours.

Thermal energy storage based on the use of the solid–liquid phase change of materials (PCM) is a technique that has been recently raising a greater practical interest. Such an interest is motivated by the great thermal energy storage density per unit volume of PCM materials in a reduced temperature range, and also by the constant incorporation of new materials with very different properties and phase change temperature intervals. The interest in phase change materials is evident when considering thermal energy storage systems with PCM, which have been developed for different applications [1].

Recently, a new technique has been proposed to use phase change materials in thermal storage systems, heat exchangers and thermal control systems. This new technique consists of forming a two-phase fluid, from the mixture of a fluid, such as water, and a phase change material, such as paraffin, resulting in a latent heat storage fluid. Inaba [2] classifies thermal fluids, describing the main characteristics and applications. Among the latent thermal fluids, five types of fluids are mentioned: 1) ice slurries; 2) phase change material microemulsions, in which the PCM is dispersed in water through an emulsifying agent; 3) microencapsulated PCM slurries, where the PCM is microencapsulated in a polymeric capsule and dispersed in water; 4) clathrate hydrate PCM slurries, where the clathrate hydrates are composed of water molecules (host molecule) forming a weaved structure where the molecules of the other substance (guest molecule) are accommodated, constituting a special molecular structure where the heat associated with the chemical reaction of formation and dissociation of clathrate hydrate is greater than that of ice melting and 5) shape-stabilized PCM slurries (ssPCM slurries), based on ssPCM, these can consist of paraffin infiltrated in high density polyethylene, with a melting temperature higher than of the paraffin. In this way the paraffin is retained inside the structure of high density polyethylene, avoiding the leak of the PCM. Fig. 1 shows a schematic draw of the different types of PCM slurries [3], although the case of clathrate hydrate PCM slurries does not appear drawn. In 2010, Zhang et al. [4] published a review, focused on two latent thermal fluid types: mPCM slurries and clathrate hydrate slurries, putting special emphasis on thermal properties and applications. The review presented herein aims at completing the work of Zhang et al. [4] regarding mPCM slurries and going a step further by analyzing the information available in literature on PCM emulsions and by studying the heat transfer phenomenon.

As main issues to be tackled, some studies inform that in the case of mPCM slurries it is particularly difficult to maintain a stable homogeneous flow if the particles are not processed with very small size and high flexibility. Besides, the PCM capsule entails an extra

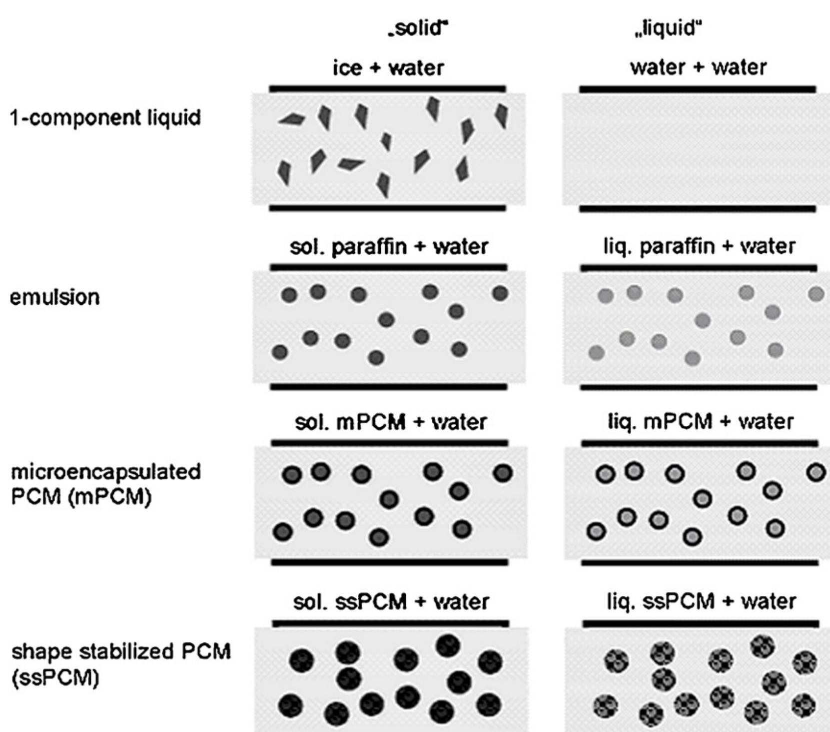


Fig. 1. Schematic drawing of the different types of PCM slurries [3].

cost. The capsule prevents the PCM in continuous phase from leaking, which in that case could solidify in ducts and cause clogging. It is important that the capsules are sufficiently resistant against the stress produced by the pumps. In the case of emulsions, previous experiments indicated that it is difficult to maintain a stable emulsion above melting temperature, as instabilities could appear during phase change [5]. Stratification problems will appear, as the paraffin droplets will form greater droplets and finally a PCM layer will float in the upper part of the storage system, due to the difference of densities [3].

These new fluids offer many advantages and can be used either as thermal storage materials or heat transfer fluids [6], due to: 1) high storage capacity during phase change, 2) possibility to use the same medium either to transport or store energy, as these slurries are pumpable (reducing in this way heat transfer losses), 3) heat transfer at an approximately constant temperature, 4) high heat transfer rate due to the elevated ratio surface/volume, 5) lower pumping power, as a consequence of the reduction in mass flow due to higher heat capacity, 6) a better cooling performance than conventional heat transfer fluids, due to the decrease in fluid temperature as a consequence of higher heat capacity. As additional advantages, these novel fluids present a thermal energy storage density that results advantageous in comparison to conventional systems of sensible heat storage in water and can be competitive against macroencapsulated PCM tanks. According to the consulted literature, macroencapsulated PCM tanks present porosity values between approximately 0.37 and 0.47 [7–9]. This means that the PCM volume together with the container system represents approximately 53–63% of the volume of the thermal energy storage system. Therefore slurries with PCM concentrations volumes of approximately 30–40% could result competitive as thermal energy storage systems. Besides, response time will be shorter using these PCM emulsions or mPCM slurries as storage material than with macroencapsulated PCM. The tanks will be simpler as there is no need to macroencapsulate, and conventional tanks can be used. Nevertheless, currently there is a lack of experience on its technical viability. In order to be advantageous, these latent fluids must meet the following requirements [10]: 1) high heat capacity, 2) phase change temperature range matching the application, 3) low subcooling, 4) high heat transfer rate, 5) pumpable, low pressure drop in pump systems, 6) stable over a long term storage, and 7) stable to thermal–mechanical loads in pump systems.

This article encompasses a review of scientific literature as well as a technical and commercial compilation of PCM emulsions and mPCM slurries regarding their use as heat transfer fluids and thermal storage materials. This article completes the review by Zhang et al. [4] with the collection of additional information on mPCM slurries and by considering PCM emulsions. Several tables present information on PCM emulsions and mPCM slurries (PCM microcapsules) studied in scientific literature, as well as commercially available products, presenting the main characteristics of the materials. This review goes a step further by making an exhaustive analysis on heat transfer phenomena in these fluids, concluding with the factors affecting the phenomena. The review is structured in five greater sections: a first section that considers the elaboration of emulsions and the different fabrication techniques for microcapsules; a second section that presents tables containing compilation of PCM microcapsules and emulsions, both in research stage and commercially available; a third section that analyzes the thermophysical and rheological properties of PCM emulsions and mPCM slurries, also considering the subcooling problem and stability of fluids; a fourth section that deepens knowledge on heat transfer phenomena; and finally, a fifth section that enumerates and describes application examples where these new fluids have been employed.

2. Manufacture process

2.1. Elaboration of emulsions

As previously explained, emulsions are systems formed by two unmiscible liquid phases, one of which is dispersed in the other in the form of droplets through substances that modify interfacial activity, denominated surfactants. In the case of emulsions, special attention must be given to viscosity and stability. The viscosity of an emulsion will increase when thickening agents are aggregated, avoiding unstabilization processes by increasing the disperse phase proportion and reducing the size of the emulsion particles. Emulsifying methods can be classified in two groups: high and low energy methods [11]. High energy methods produce coarse emulsions (5–100 μm) through a high degree of shearing generated by helix or turbine mixers. A greater reduction in the droplet size requires a great amount of mechanical energy. The formation of nanoemulsions using high energy methods is usually very expensive, as it requires the use of high pressure homogenizers, ultrasonic generators, microfluidizers, etc. The low energy methods are those where the energy required to form the emulsion originates from transitions or phase changes occurring during the production of the emulsions.

2.2. Fabrication of PCM microcapsules

The microencapsulation technique has been widely used in the pharmaceutical and chemical engineering fields. In recent years this technology has reached the field of phase change materials in order to improve their behavior. Microcapsules are small particles of material coated by another material, the second material forming a thin film over the first one, isolating and protecting from the environment. Size range of microcapsules is quite wide, with diameter slurry between 2 and 2000 μm. The size of the shells oscillates between 0.5 and 150 μm thickness and the core constitutes between 20 and 95% of the total mass. There are many different fabrication techniques for microcapsules, and the choice is made depending on the characteristics of the active material to be encapsulated and the type of polymeric material used as shell [12].

In a first stage, a dispersion is formed with the active material. In a second stage, this dispersion is transformed and finally, stabilization and solidification techniques are applied to the shells before separation. Emulsifying techniques are, in principle, the most simple and extended for the obtaining of microcapsules.

There are several methods that can be used to produce microcapsules. Depending on the nature of the process, there are physical, physical–chemical, and chemical processes. The most utilized techniques in literature for PCM microencapsulation according to the aforementioned classification are: for the first group, the spray drying technique; for the second group, coacervation; and for the third group, in situ and interfacial polymerization. These techniques are explained in the following paragraph.

The spray-drying technique is based on the preparation of an emulsion, dispersing the material of the core (in this case the PCM) in a concentrated solution of the material forming the capsule, until the desired particle size is obtained. This emulsion is pulverized into droplets, which will be next dried when makes contact with a hot medium, evaporating the present water instantly, and consequently allowing the active material to be trapped inside a film of encapsulating material. In the coacervation technique, the polymeric solute is separated in the form of small liquid droplets (forming the coacervate) and deposited around the insoluble particles dispersed into a liquid. These droplets slowly unite and form a continuous cover around the core. In order to obtain a longer lifetime of microcapsules, coacervation can be accomplished in two steps, adding the polymer twice. Through this mechanism, a

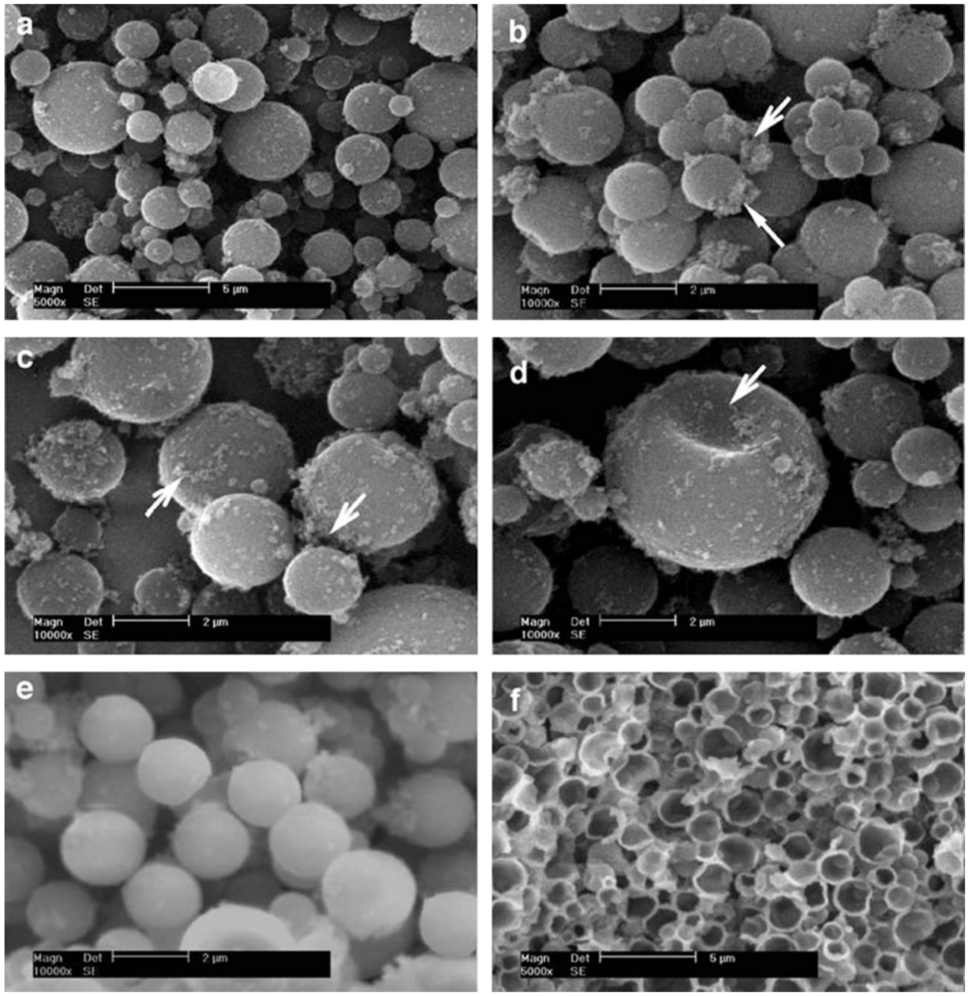


Fig. 2. Morphology of microcapsules through a SEM microscope [13].

smaller thickness of the microencapsulate shell can be obtained with the same weight index, during a longer time so that the polymer regulates its molecules with the PCM core. Compactability and impermeability are improved (a lower speed of polymer deposition increases impermeability), proportioning greater stability to the microcapsules, conserving size and spherical form. The texture is smoother and the spherical form is more regular, compared to one-step coacervation, where microcapsules with many protrusions, rougher, coarser and more porous are obtained [13]. The morphology can be observed in Fig. 2. In the interfacial polymerization technique, the polymer constituting the microcapsule cover is formed from two monomers in separate phases (an aqueous phase and an organic phase) that react in the interface of both phases, at the moment of microencapsulation. In the in situ polymerization, firstly a PCM emulsion is prepared and then the synthesis of the prepolymer solution is carried out through the mixture of two polymers, which will form the cover, and water. This prepolymer is added to the emulsion in the form of droplets, while the emulsion is agitated during a specific time. The emulsion is cooled and filtered, obtaining the microcapsules, which have to be dried.

According to the study of Yang et al. [14], the polymers that present the best characteristics at the time of microencapsulation are the flexible plastics, such as the Polymethyl methacrylate (PMMA) and polyethyl methacrylate (PEMA). With these plastics, a higher value of melting and solidification latent heat is achieved. Besides, the viscosity of the slurry is not significantly affected by the material of the microcapsule shell. The main manufacturer of PCM microcapsules and mPCM slurries is BASF. BASF manufactures its microcapsules from a polymerization process of a PCM emulsion. This microencapsulation process can be observed in Fig. 3 [15]. Firstly a paraffinic emulsion is elaborated in hot water with agitation and detergents. Then the monomers are added and the growing process of the polymeric capsule begins in the interface of paraffin and water. Finally a highly-reticulated polymer forms a dense capsule over each paraffin droplet. This process results in a liquid product, in which the capsules are dispersed in water. The microcapsules are obtained after the dispersion passes through a drying tower, as shown in Fig. 4. The diameter of the dispersion microcapsules is between the range 2–20 μm. Nevertheless, after the drying process, secondary particles with a larger size are created.

3. Compilation table of PCM emulsions and mPCM slurries

Table 1 shows information on the PCM microcapsules and mPCM slurries studied in literature, together with some thermophysical properties, as well as additional interesting information given by the authors. Table 2 shows a compilation of PCM emulsions studied in literature.

At the moment there are few PCM manufacturers approaching these techniques. Table 3 collects data on commercially available PCM emulsions, mPCM slurries and PCM microcapsules up to date.

As is known, inorganic PCM, usually salt hydrates, present certain advantages when compared to organic PCM, such as a higher energy storage density, higher thermal conductivity,

Table 1
PCM microcapsules and mPCM slurries studied in literature.

Ref.	Microencapsulation process	Core material	Shell material	Nucleation agent	Size distribution	Melting temperature	Phase change enthalpy
[13]	Two step coacervation	n-Octadecane	Melamine formaldehyde		2 μm		
[14]	In situ polymerization	Tetradecane	1) PVAc (polyvinyl acetate) 2) PS (poliestirene) 3) Polymethyl methacrylate (PMMA) 4) Polyethyl methacrylate (PEMA) Tetradecane content of capsule: 40%		2) 5–40 μm 3) 5–30 μm 4) 5–30 μm	1) No manisfested phase change 2) 2.06 °C 3) 5.97 °C 4) 5.68 °C	2) ∼0 3) 66.26 kJ/kg 4) 80.62 kJ/kg (melting enthalpy)
[16]		Lauryl alcohol	Melamine formaldehyde		5–10 μm	24 °C	
[17]		n-Octadecane			1–2 μm Ø average: 1.3 μm		
[18]	Interfacial polymerization	n-Octadecane	Poliurethane		5–10 μm		
[19]	Interfacial polymerization	n-Octadecane n-Nonadecane n-Eicosane	Urea Melamine formaldehyde	l-Tetradecanol paraffin l-Octadecanol			160 kJ/kg
[20]	In situ polymerization	n-Octadecane	Urea Melamine formaldehyde		0.2–5.6 μm		
[21]	In situ polymerization	Paraffin	Urea-formaldehyde		5–20 μm (depending on the amount of emulsifier)	∼54 °C	157.5 kJ/kg (76.9% core content) (melting enthalpy)
[22]	Polymerization of emulsion	Docosane	PMMA (polymethyl methacrylate)		0.14–0.466 μm Ø average: 0.16 μm	41 °C	54.6 kJ/kg
[23]	In situ polymerization of a nanoemulsion assisted by ultrasound	n-Octadecane	Poliestirene		50–200 nm Ø average: 124 nm		124.4 kJ/kg
[24]	In situ polymerization	n-Octadecane	Melamine formaldehyde			30.5 °C	170 kJ/kg (melting enthalpy)
[25]	Polymerization	n-Octacosane	PMMA (polymethyl methacrylate)		0.15–0.33 μm Ø average: 0.25 μm	50.6 °C	86.4 kJ/kg
[26]	Coacervation Spray-drying	Paraffin wax (Merck)					145–240 kJ/kg (depends on the ratio core/shell and on the method)
[27]	In situ polymerization	n-Octadecane	Melamine formaldehyde		Ø average: 2.2 μm	40.6 °C	144 kJ/kg
[28]	Coacervation	1) 99.8% Tetradecane + 0.2% silica fume 2) 98% tetradecane + 2% tetradecanol 3) 94% tetradecane + 6% tetradecanol	Gelatin	Silicon fume Tetradecanol	1) 90–150 μm Ø average: 100 μm 2) 70–260 μm Ø average: 145 μm 3) 2–10 μm Ø average: 4.4 μm		3) 202.1 kJ/kg (melting enthalpy)
[29]		n-Octadecane			1–5 μm Average diameter 4.97 μm	Melting range: 24–29 °C	147.1 kJ/kg (melting enthalpy)
[30]		l-Bromohexadecane	Amino plastic Ratio core–shell: 7 Capsule thickness: 0.3 μm		Average diameter: 8.2 μm	14.3 °C (melting starting temperature)	5 wt% 6.5 kJ/kg 10 wt% 13 kJ/kg 15.8 wt% 20.5 kJ/kg (melting enthalpy)
[31]		RT6				Melting range: 4–6.8 °C	For a 45 wt% concentration: 55 kJ/kg (melting enthalpy)
[32]		DPNT06-0182 (Ciba Specialty Chemicals)			10–100 μm	∼35 °C	96.968 kJ/kg 10% 8.074 kJ/kg 25% 15.194 kJ/kg 35% 37.213 kJ/kg (melting enthalpy)
		Micronal DS 5008X (BASF)			1–20 μm	∼29 °C	102.008 kJ/kg

Table 2
PCM emulsions studied in literature.

Ref.	PCM	Nucleation agent	Surfactant	Emulsifying method	Size distribution	Melting temperature	Phase change enthalpy
[5]	Mixture of n-alkanes		Non-ionic surfactant	Ultrasonic generator Power: 500 W Frequency: 20 kHz	2 μm	9.5 °C	50% 78.9 kJ/kg (melting enthalpy)
[11]	20% Tetradecane		6% surfactant (67.7% Tween60, 32.3% Span60)	Phase inversion temperature method	200–250 nm		43 kJ/kg (melting enthalpy)
[14]	Tetradecane				Average diameter 10% 18.18 μm 20% 18.56 μm 30% 16.05 μm	10% 5.06 °C 20% 5.84 °C 30% 5.84 °C	10% 18.5 kJ/kg 20% 112.3 kJ/kg 30% 150.8 kJ/kg (melting enthalpy)
[33]	Hexadecane				<0.1 mm	16.5 °C	
[34]	C22H46				10–40 μm		
[35]	Mixture of hexadecane and tetradecane 70/30						
[36]	30% RT6, RT10, RT20	2.5% paraffin with a melting temperature of 50 °C	1.5% alcohol ethoxylate				For a temperature range of 6 °C and 30 wt% concentration: RT6 = 75 kJ/kg RT10 = 50 kJ/kg RT20 = 44 kJ/kg (total capacity of storage)
[37]	Hexadecane		- SDS - Tween	- Disperser - Ultrasonic generator	0.05–30 μm (depending on the method)		
[38]	- tetradecane - hexadecane - RT20		- SDS - Tween40 - Surfactant mixture	- Ultrasonic generator - Rotor-stator system	0.05–30 μm (for the hexadecane emulsion depending on the method)	15.4–17.4 °C (for the hexadecane emulsion)	
[39]	Paraffin			Phase Incursion Method	Average diameter: 0.304 μm		
[40]	30% RT 10					Melting range: 4–11.5 °C	55 kJ/kg (5–11 °C) (total capacity of storage)

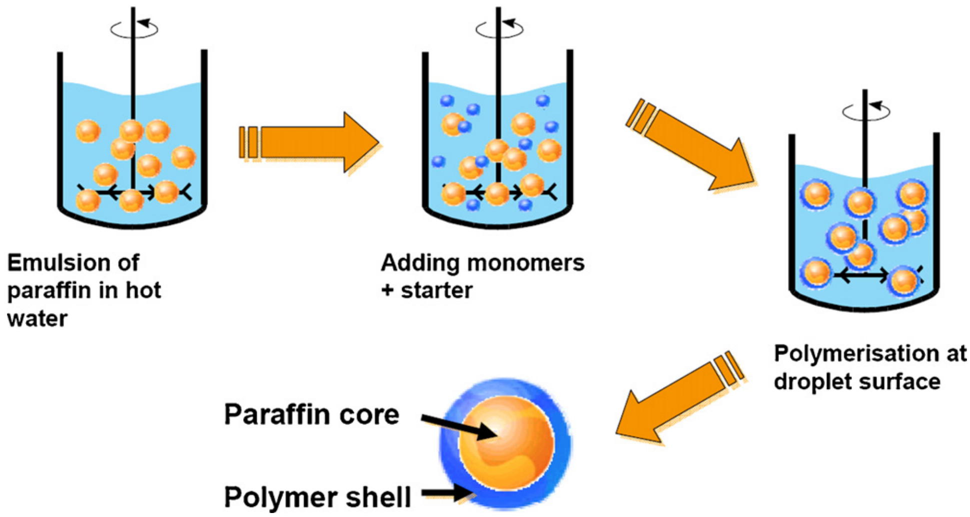


Fig. 3. Microencapsulation process of BASF [15].

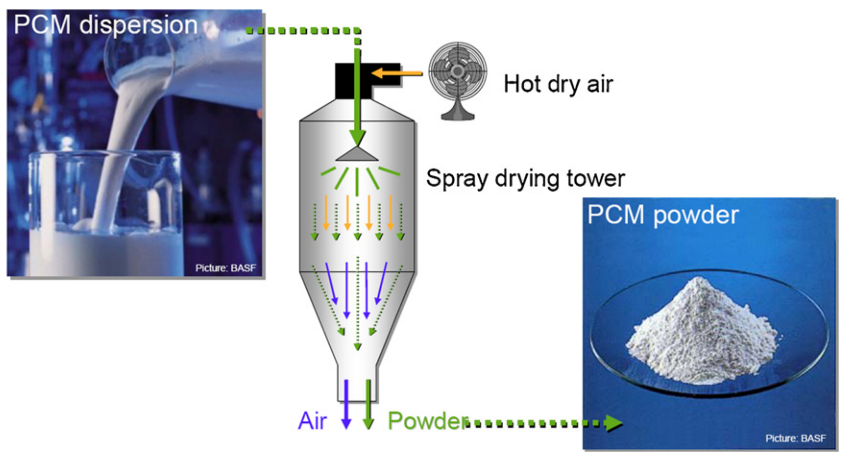


Fig. 4. Drying process of BASF [15].

non-flammability, and are cheaper. Nevertheless, inorganic PCM also present a series of inconveniences, such as the corrosion problem, phase segregation and subcooling. As a consequence of this last problem (which in microscopic geometries would be worse due to probabilistic reasons), there are still few studies on inorganic PCM microencapsulation. After systematic reviews, the only manufacturer of inorganic microencapsulated PCM is Capzo, selling microcapsules of salt hydrates and the only consulted work is that of Salaün et al. [41]. This last work investigates the effects of the preparation conditions (solvent evaporation–precipitation process) on the morphology of the capsule and on the efficiency of the sodium phosphate dodecahydrate encapsulation.

Table 3
Commercially available PCM microcapsules.

Manufacturer	Product	Type of product	PCM	Concentration	Particle/droplet size	Melting temperature	Latent heat
BASF	DS 5000	mPCM slurry	Paraffin	42%		26 °C	45 kJ/kg
	DS 5007	mPCM slurry	Paraffin	42%		23 °C	41 kJ/kg
	DS 5030	mPCM slurry	Paraffin	42%		21 °C	37 kJ/kg
	DS 5001	Powder	Paraffin			26 °C	110 kJ/kg
	DS 5008	Powder	Paraffin			23 °C	100 kJ/kg
	DS 5030	Powder	Paraffin			21 °C	90 kJ/kg
Microtek Laboratories	MPCM-30D	Powder	n-Decane		17–20 μm	−30 °C	140–150 kJ/kg
	MPCM-10D	Powder	n-Dodecane		17–20 μm	−9.5 °C	150–160 kJ/kg
	MPCM 6D	Powder	n-Tetradecane		17–20 μm	6 °C	157–167 kJ/kg
	MPCM 18D	Powder	n-Hexadecane		17–20 μm	18 °C	163–173 kJ/kg
	MPCM 28D	Powder	n-Octadecane		17–20 μm	28 °C	180–195 kJ/kg
	MPCM 37D	Powder	n-Eicosane		17–20 μm	37 °C	190–200 kJ/kg
	MPCM 43D	Powder	Paraffin mixture		17–20 μm	43 °C	100–110 kJ/kg
	MPCM 52D	Powder	Paraffin mixture		17–20 μm	52 °C	120–130 kJ/kg
Capzo	Thermusol HD35SE	Powder	Salt hydrate			30–40 °C	200 kJ/kg
	Thermusol HD60SE	Powder	Salt hydrate			50–60 °C	160 kJ/kg

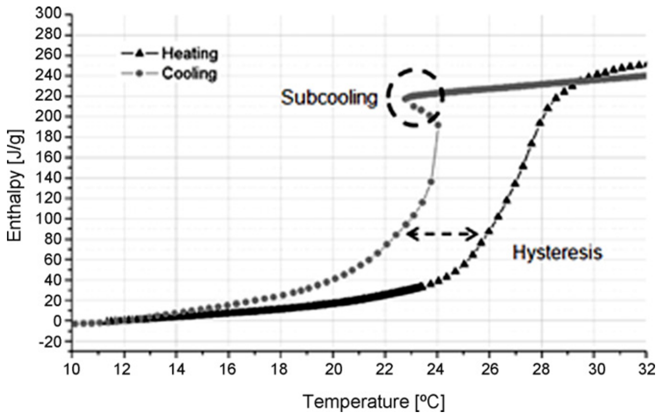


Fig. 5. Hysteresis and subcooling phenomena.

4. Main characteristics of PCM emulsions and mPCM slurries

4.1. Solidification, hysteresis and subcooling

When different results between the measurements of the cooling and heating processes are obtained, this phenomenon is called hysteresis; nevertheless, hysteresis is commonly understood as a material property. The effects (due to the measurement conditions) are called apparent hysteresis. In the case of inorganic materials the hysteresis phenomenon is much more noticeable than in the case of organic materials.

There are several effects that originate hysteresis due to the material, and the most common is subcooling. When a liquid has to be cooled to a temperature below its melting temperature so that the crystallization process to begin, this process is called subcooling. Subcooling is always a serious issue in PCM investigation and application fields, as the operation temperature range of the storage systems will be wider, worsening the energy efficiency of the systems. Despite the fact that many PCM do not present the subcooling phenomenon in macroscopic geometries, the problem occurs in microscopic geometries. The hysteresis and subcooling problem can be observed in Fig. 5.

Phase transformation, in this case solidification, can be described as a nucleation process and posterior growth of the stable nuclei formed. Depending on the nature of the material and on the transformation, two types of nucleation can occur: homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs if all volumes of the initial phase are identical from energy, chemical, and structural viewpoints. This is not the most common process as materials inevitably contain defects or non-homogeneities that cause local differences in some properties. In this case nucleation will occur preferably in those locations where non-homogeneities occurred. The process ceases to be random as there are preferential nucleation locations and then heterogeneous nucleation takes place. In heterogeneous nucleation the formation of nuclei begins in preferential locations such as walls or imperfections. The addition of impurities such as nucleation elements is a technique used to obtain greater homogeneity in the structure of the solidified material. The aggregation of particles that act as nucleation agents can result in solidification at lower subcooling, avoiding the formation and growth of nuclei mainly from the walls of the mold, and leading to structures with anisotropic behavior. In his experimental work, Huang et al. [36] utilized paraffin as a nucleation agent, with a higher melting temperature than the material in solidification, obtaining in this way solid surfaces on which to begin the solidification process. Nevertheless, due to the microscopic size of particles in the case of PCM emulsions and mPCM slurries, the probability that nucleation agents are present to begin the solidification process of the PCM is lower, and therefore a lower temperature is required for solidification to start. This effect is explained by Günther et al. [37] in her article. For a given concentration of seeds, the number of active volumes (droplets) by these seeds is dependent on the size of the volumes. The remaining inactive volumes (droplets without seeds) can only solidify after homogeneous nucleation. The fraction of active volumes with respect to the inactive volumes in function of the size of the element corresponds to a Poisson distribution.

There are many authors that have studied the subcooling problem in PCM emulsions and mPCM slurries as well as the way to eliminate such problem. The authors of the different studies consider the value of subcooling as the difference between the peak temperatures in the heating curve and in the cooling curve, obtained with the DSC.

In the case of the paraffin emulsion developed by Huang et al. [10], in order to prevent subcooling, a nucleation agent was added to the paraffin before the emulsifying process. The nucleation agent offered the necessary surface to start nucleation in the interior of the paraffin droplets, acting therefore as a nucleation catalyser. The emulsion without nucleation agents presented a 7 °C subcooling, while with the addition of the nucleation agent it was reduced to 0.1 °C. To study the effect of the droplet size on the nucleation and subcooling, Huang et al. [38] prepared different paraffin-in-water emulsions with various droplet sizes. They found that besides the droplet size, the surfactant of the emulsion had a significant influence on the solidification. They also observed that all emulsions containing nucleation agents showed a freezing peak spectrum. In the second part of this paper [42], Günther et al. discussed possible interpretations of the observations according to the nucleation theory. They relate the increased subcooling in emulsions to the droplet size. The seed deactivation for a given seed concentration increases when the droplet size decreases. Regarding to the surfactants, they point out that their chemical structure could promote the nucleation. They also mention that while in larger droplets (low curvature), the alignment of the surfactants tails is almost parallel, offering in this way a pattern for crystallization of the alkane crystal, in smaller droplets (high curvature) this alignment is more complicated. The freezing peak spectrum is explained with different seed types, as it can be observed in Fig. 6. In a bulk sample, nucleation is dominated by primary seeds (dots), at their nucleation temperature T_1. When the volume is divided into droplets, secondary seeds (squares) become active at T_2. For smaller droplets, nucleation on the droplets wall or homogeneus nucleation comes into the play at T_3. Alvarado et al. [43] studied the subcooling process in n-tetradecane microcapsules, as well as its elimination due to the addition of nucleation agents. N-tetradecane microcapsules were prepared with gelatine capsules, producing microcapsules with an average diameter of 100 μm, utilizing two different substances and concentrations as nucleation agents (0.2% silica, 2 and 4% tetradecanol). Silica fume did not result adequate as a nucleation agent. A concentration of 2% tetradecanol resulted sufficient to suppress subcooling both in tetradecane and microencapsulated tetradecane, suggesting that heterogeneous nucleation was more favourable in the presence of tetradecanol. Nevertheless the amount of nucleation agent should be the smallest possible in order to eliminate subcooling and reduce by the least the melting latent heat. Zhang et al. [19] also investigated crystallization from a DSC for the n-octadecane microencapsulated with l-octadecanol as a nucleation agent. The cooling curves obtained from the DSC for the microencapsulated n-octadecane were mainly affected by the average diameter of particles. The maximum degree of subcooling was 26 °C with a cooling/heating rate of the DSC of 10 °C/min. An addition of 10% in weight of l-octadecanol inside the microcapsules as a nucleation agent decreased subcooling from 26 °C to

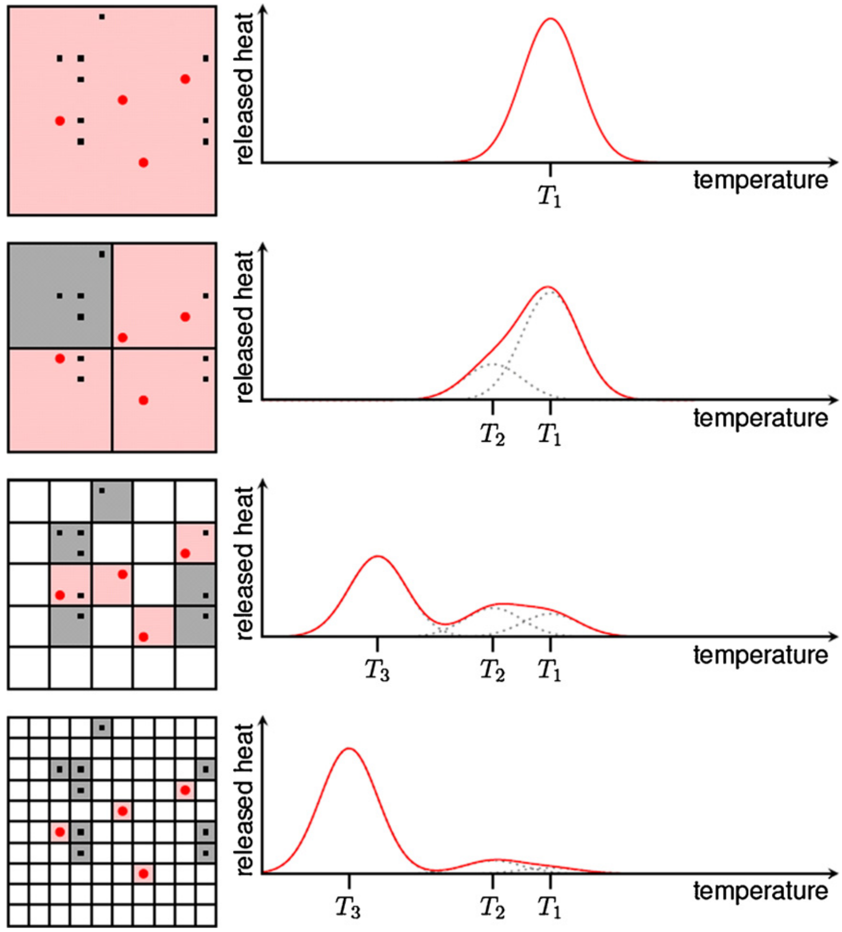


Fig. 6. Effect of two different types of seeds on the nucleation process [42].

12 °C with a DSC rate of 10 °C/min. Yamagishi et al. [44] evaluated two n-tetradecane and n-dodecane microencapsulated slurries and observed that despite the fact that bulk PCM did not present subcooling, it was detected in the microcapsules. In the particle size range between 5 and 100 μm, the crystallization temperature decreased along with particle size. l-Tetradecanol was added as nucleation agent and it cancelled subcooling. Griffiths and Eames [45] studied the behavior of a chilled ceiling through which a mPCM slurry circulated. The DSC curves indicated that if the PCM was completely melted before being cooled, the mPCM slurry showed a subcooling of 5 °C. Nevertheless the experimental observations and the DSC indicated that if the mPCM slurry was cooled before complete melting of the PCM, the presence of solid material acted as a nucleus, and therefore the PCM solidified at higher temperatures. For this reason lower outlet temperatures than those of complete melting of the PCM were used.

4.2. Stability

4.2.1. Stability of PCM emulsions

The stability question is always a concern during the development and production of an emulsion. There are five main instability problems [46]:

- Creaming or sedimentation, as a result of gravity if there are density differences between disperses and continuous phases. In an O/W emulsion (oil/water), creaming is the movement of the oil droplets due to gravity, causing a concentrated layer at the superior part of the sample. Sedimentation is the opposite process.
- Flocculation, the process of agglomerating the emulsion droplets.
- Coalescence, process through which two or more droplets of the disperse phase melt and form a bigger droplet.
- Ostwald ripening, as a result of solubility differences of the disperse phase contained in droplets of different sizes.
- Phase inversion, process through which the continuous phase converts itself into the disperse phase and the disperse phase converts itself into the continuous phase.

Creaming, sedimentation and flocculation are not accompanied by a change in size distribution of the disperse phase, while coalescence and Ostwald ripening cause an increase in the size of the droplet. Fig. 7 shows the instability processes mentioned.

In a stable emulsion, the aforementioned instability processes never occur. However, the majority of emulsions inherently tend to separate, especially under complex operation conditions. Many studies analyze the stability of emulsions, which is of vital importance in the future use of emulsions as thermal storage materials. It is also important that thermal properties remain invariable after thermal cycling. Huang et al. [10] observed that, after a one-month storage period of a RT 10 emulsion (paraffin from Rubitherm), emulsions with a 15–60% weight concentration presented creaming, while emulsions with a 60–75% concentration did not present instability. After one year, no changes in size distribution of particles were detected and the emulsions maintained their heat capacity. Under mechanical–thermal loads, the droplet size of the paraffin emulsion suffered a slight increase in size. Besides, the nucleation agents of the paraffin droplets separated, showing a marked subcooling. The viscosity curves were similar before and

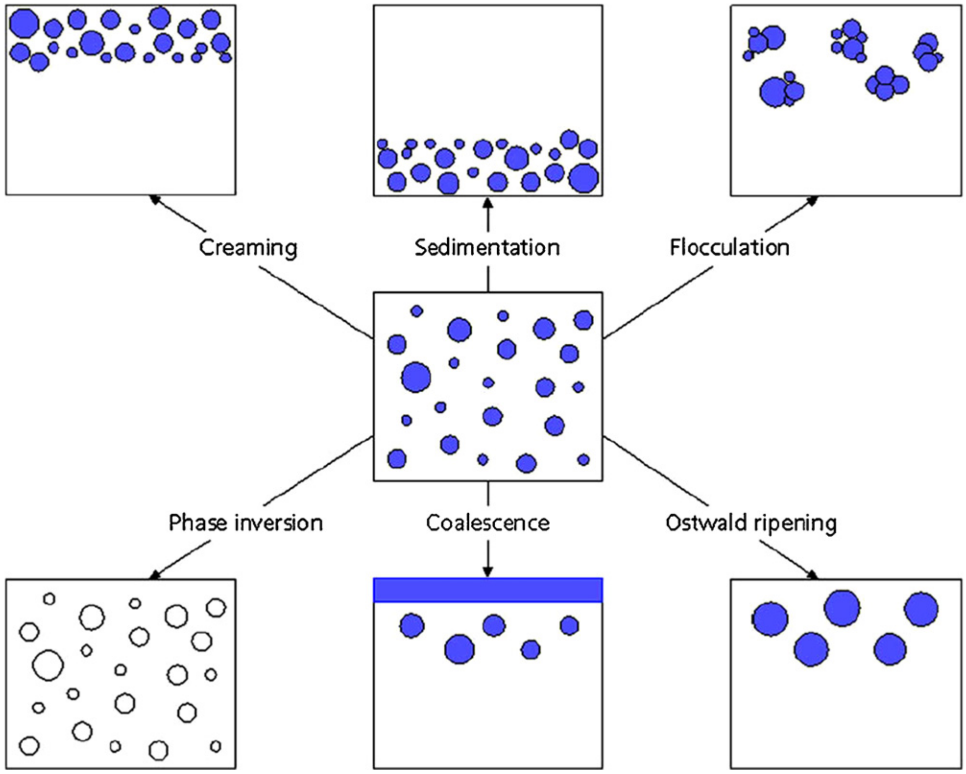


Fig. 7. Instability processes in emulsions [10].

after the tests and the heat capacity was maintained. Choi et al. [47] investigated the possibility of using an emulsifier to generate PCM droplets, specifically of hexadecane, which would not adhere to each other. The amount of emulsifier must be above a critical value in order to obtain emulsions with uniform and stable droplets. The emulsifier affected also the dynamics of the interface between an exchanger surface and the PCM, establishing whether hexadecane adhered to the surface. The project of Lorsch et al. [35] was carried out to determine the feasibility of applying a series of emulsions with paraffin mixtures hexadecane/tetradecane 70/30 in chillers, specifically to study the risk of clogging the pipes with these new heat transfer fluids. This agglomeration was more probable when the droplet size increased during the solidification processes. Previous investigations have established that when the size of the droplet was below 0.1 mm, the pipes did not clog. This droplet size could be controlled through the amount of surfactant. Zou et al. [39] describe how agglomeration or precipitation processes can be avoided by: 1) reducing the diameter of the PCM droplets, as a very small droplet size causes a reduction in gravity force and the Brownian movement can be sufficient to compensate for gravity. The droplet size can be reduced through the optimization of emulsifying conditions, such as surfactant agents, their concentration, agitation speed, duration of emulsification, etc. 2) searching for a reasonable concentration of PCM. Schalbart et al. [11] prepared several PCM nanoemulsions using different emulsification routes from low energy emulsification methods (phase inversion temperature method), determining the best emulsification routes to obtain satisfactory stability in the resultant emulsions.

4.2.2. Stability of mPCM slurries

In the case of mPCM slurries, problems such as sedimentation, creaming or agglomeration can also occur, but the main problem is microcapsule rupture. Yamagishi et al. [44] studied the damage produced by the stresses caused by the pump or by agitation on microcapsules. They observed that agitation did not damage microcapsules and when suffering stresses caused by the pump, the rupture index decreased along with particle size. Regarding thermal cycling (contraction–expansion), it was observed that the 5 μm microcapsules did not rupture and the thermal properties of cycled microcapsules remained invariable. Zhang et al. [20] studied the influential factors on thermal stability in relation to the structure of n-octadecane microencapsulated into urea melamine formaldehyde capsules. A loss of liquid n-octadecane from the microcapsule was observed due to microcapsule rupture, as a consequence of a bad adjustment of core and capsule expansion at high temperatures. Zhang et al. [24] investigated the effects of several parameters of the microencapsulation process on the properties and stability of n-octadecane microencapsulated and nanocapsulated into melamine formaldehyde capsules. The thermal stability of the microcapsules and nanocapsules increased along with the increase in agitation speed and with the emulsifier content. Gschwander et al. [48] built an experimental setup to cycle different mPCM slurries. The mPCM slurries were pumped during several weeks in order to study stability. Conventional components such as expansion valves, heat exchangers, etc., worked well with mPCM slurries. The stability of microcapsules was negatively affected by high shearing speeds, which occurred mainly in the pump. After testing several pumps, the centrifugal pumps resulted in less damage or less destruction of the microcapsule shell. The good stability of capsules was a result of a smaller diameter and a thicker shell. This configuration resulted in a smaller fraction of paraffin and therefore a lower melting enthalpy. The microcapsules could be pumped during weeks, which resulted into a period equivalent to years in a real installation (800 cycles per day). Fan et al. [17] synthesized and studied in detail the thermal stability and permeability of microencapsulated n-octadecane and cyclohexane. The content of cyclohexane in the core has a remarkable effect on morphology, thermal stability and permeability. After thermal treatment of capsules, the volatile character of cyclohexane caused an expansible space to be formed, which improved the

thermal stability of microcapsules. These microcapsules presented a greater resistance to temperature and less mass loss. This weight loss was attributed mainly to the loss of n-octadecane in some broken capsules. Alvarado et al. [28] presented thermophysical properties of a microencapsulated tetradecane slurry. In concrete, with respect to microparticle stability, it was observed that the size of the microcapsule should be smaller than 20 μm to avoid rupture. If a considerable amount of microcapsules were broken during durability tests, smaller capsules or capsules with a higher thickness/diameter ratio were tested. Microcapsules with a 2–10 μm diameter showed less damage during circulation through a progressive pump. Jin et al. [21] prepared and studied the behavior of paraffin microcapsules with a phase change temperature of 50.2 °C, specifically the influence of the weight percentage with respect to the PCM core on the stability during phase change. They observed that the microcapsules suffered coalescence when the content of the capsules was inferior to 2.1% in weight as a consequence of microcapsule rupture. When the content of the capsule was 16.7% in weight, the microcapsules suffered partial coalescence. When this percentage increased to 28%, the capsules remained intact after an elevated number of thermal cycles and presented a better thermal stability than bulk paraffin. Alkan et al. [22] characterized the behavior of docosane microencapsulated into PMMA (polymethyl methacrylate) capsules, which were synthesized by them. Degradation of bulk docosane took place in a single stage at a temperature of approximately 120 °C, while microcapsules degraded in two stages: at 240 °C and at 323 °C. No significant changes were observed in the temperature or phase change enthalpies, after thermal cycles (1000, 3000, and 5000 cycles). Griffiths and Eames [45] pumped a mPCM slurry through a chilled ceiling. During the experiments, deposition of microcapsules was not observed in the pipe elbows and around valves. Degradation of the slurry was not observed either. It was observed that dry pumps were adequate to pump the slurry.

From this review on the stability of PCM emulsions and mPCM slurries it can be concluded that, for the case of PCM emulsions and mPCM slurries, the creaming phenomenon and microcapsule rupture are the most frequent problems. In the case of emulsions, the creaming problem can be solved through the reduction of the PCM droplet size. In the case of the mPCM slurries, microcapsule rupture is solved through the reduction of particle size and/or increase of the relationship thickness capsule/thickness core for the PCM.

4.3. Rheological behavior, viscosity and pressure drop

The viscosity measurement and rheological characterization of these slurries systems, PCM emulsions and mPCM slurries, must be taken into account as although it seems homogeneous at a macroscopic level, the presence of other phases at a microscopic level modifies their behavior significantly. The concept of viscosity is based on the supposition that fluids are homogeneous and that, as a consequence, can be treated as continuous. Nevertheless, disperse systems exhibit a behavior that diverges strongly from the behavior observed in homogeneous fluids. This is due to the presence of two or more phases, which generates one or more interfaces of different nature. As a consequence, the behavior of the flow can range from simply Newtonian in diluted particle systems with no interaction, to highly non-Newtonian behaviors in concentrated or diluted systems where there is elevated interaction between particles. The main physical properties that influence rheological behavior are the content of the disperse phase; size, form and distribution of particle size and temperature. For the case of emulsions, two other factors must also be considered: degree of droplet deformation and disperse phase viscosity [49].

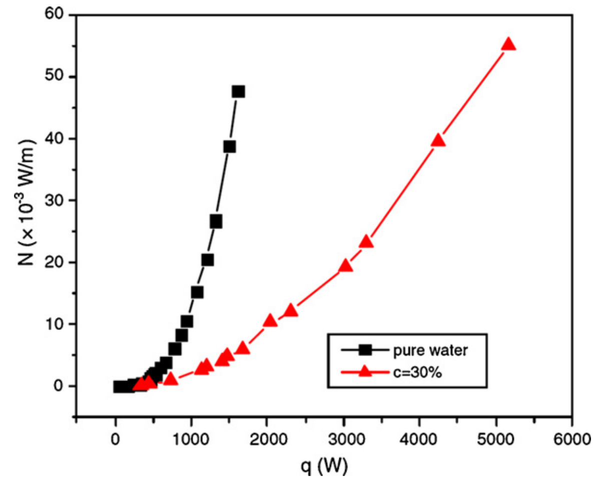


Fig. 8. Relationship between pumping work and heat transfer [50].

4.3.1. Rheological behavior of PCM emulsions

Choi et al. [33] observed that in their 10% hexadecane emulsion, pressure drop decreased significantly starting from the melting point of PCM particles. The focus of the work of Royon et al. [5] was on the study of the thermorheological behavior of an emulsion with a 50% n-alkane concentration in weight. The results of the rheological experiments showed a pseudoplastic behavior and the apparent viscosity of the emulsion followed the power law. Viscosity decreased with the increase of temperature and the n and k indices were functions of temperature. The k index decreased with an increase in temperature, and the relationship between the k index and temperature was exponential. The n index showed a slight rise close to 9.5 °C (phase change temperature), mainly caused by the phase change of the component in dispersion. Chen et al. [50] built an experimental installation to study the rheological characteristics of a tetradecane emulsion with a weight concentration of 30%, prepared by the phase inversion temperature method. The emulsion could be considered a Newtonian fluid. The friction factor was adjusted to the classical function $f = 64/Re$ for laminar flow. Viscosity of the emulsion was 5.57 times that of water. The flow and pump work decreased considerably for the same amount of heat transfer when compared to water, due to phase change, as can be seen in Fig. 8. Pollerberg and Dötsch [51] presented the comparison of three slurries systems in distribution system applications: ice slurries, tetradecane emulsion, and microencapsulated tetradecane slurry. One of the points studied was the rheological behavior of these slurries. The emulsion shows a Newtonian behavior in a weight concentration range of 10–20% and its viscosity was between 2 and 8 times that of water, depending on the tetradecane concentration. Both the slurry and the emulsion caused a higher pressure drop than water in laminar flow. Nevertheless, the pressure drop curves overlap in turbulent regime. All samples prepared by Huang et al. [10] presented a pseudoplastic behavior. The K and n coefficient of the power law ($\tau = K \cdot \varphi^n$) were practically constant with a weight fraction of 15–50%. A decrease in n and an increase in K were observed when concentration exceeded 50%. Besides, viscosity increased with the increment of solidified fraction. One reason for this behavior is that the solid droplets were not suffering significant deformation, resulting in a higher viscosity than when the droplets were melted. A working limit fraction was established at 50%. Huang et al. [36] observed a pseudoplastic behavior in their PCM emulsions, in which viscosity decreased along with shear rate and then tended to remain constant when shear rate was higher than 30 s^{-1}. Temperature influenced significantly, especially phase change. The reason for this phenomenon could be that the solid particles were not very deformed by shearing, causing a higher

viscosity than that of liquid droplets. Cho et al. [52] observed that the increase in pumping work in the case of their emulsion with a 25% volumetric concentration of PCM was small in the turbulent region, in comparison to water. In the case of the emulsion of Lorsch et al. [53], a fraction of volume up to 20% increased the pressure drop only by 3% compared to water. When the mixture was cooled to a temperature below PCM solidification, the pressure drop increased from 3 to 5%. Zou et al. [39] verified that for a given PCM concentration, there is a flow rate that causes the greatest savings in pumping consumptions.

4.3.2. Rheological behavior of mPCM slurries

Yamagishi et al. [44] studied the feasibility of n-tetradecane and n-dodecane microencapsulated slurries in low temperature applications. One of the studied aspects was the viscosity of these slurries. Specifically, viscosity was measured by a cylindrical Couette viscometer and it was observed that apparent viscosity depended on several parameters: PCM concentration, temperature of slurry, and microcapsule size. When adding addictives such as surfactant agents, the slurry stopped behaving as a non-Newtonian fluid and started behaving as a Newtonian fluid. Yang et al. [14] prepared slurries with microencapsulated tetradecane from different materials and observed that the capsule material did not influence the viscosity of the sample. Rao et al. [54] centered their study on the flow characteristics of microencapsulated n-octadecane slurries with concentrations from 5 to 20%, circulating through horizontal minichannels. The friction factor of the slurries under laminar regime increased along with the PCM concentration. Compared to the friction fraction of water, a slight increase was observed in low-concentration (5%) slurries. Nevertheless, when concentration was 10% or higher, the increment in friction factor was more marked. The increment in PCM concentration of the slurries tended to suppress the generation of turbulence in the flow. When concentration was at least 15%, no obvious transition was observed from laminar to turbulent flow as occurred in low-concentration PCM at Re = 2000. The pressure drop of the mPCM slurries flowing through the minichannels increased throughout the speed range when concentration increased. As previously mentioned, Pollerberg and Dötsch [51] compared an ice slurry, a tetradecane emulsion and a microencapsulated tetradecane emulsion. The slurry presented the behavior of a pseudoplastic fluid, and viscosity was between 120 and 550 times that of water. Both the mPCM slurry and the PCM emulsion studied in this work presented a higher pressure drop than water in laminar regime. Nevertheless, the pressure drop curves overlapped in turbulent regime. In the microencapsulated tetradecane slurries developed by Alvarado et al. [28] with concentrations oscillating between 5 and 17.7%, the relative viscosity seemed to be independent of temperature (in the phase change temperature range) for all concentrations. The slurries behaved as a Newtonian fluid, until mass fractions of 17.7%. The results also indicated that the pressure drop increased slightly when PCM microcapsules were used, but did not affect significantly the pumping work. In some cases the pressure drop was lower than water, maybe due to a possible rupture of microcapsules and liberation of phase change material. The viscosity of the slurries prepared by Wang et al. [55] with concentrations ranging from 5 to 27.6% of l-bromohexadecane adjusted to the values predicted by the Vand model. All slurries presented a Newtonian behavior. The pressure drop measurements showed a marked transition when the flow changed from laminar to turbulent flow. The friction factors in turbulent flow adjusted well to the classic Hagen Poseiuille model, while the friction factors in laminar flow were lower than those calculated with the Blasius equation, as observed in Fig. 9. In the experimental work of Heinz and Streicher [56], it was observed that with a concentration up to 30%, the pressure drop was not considerably higher that

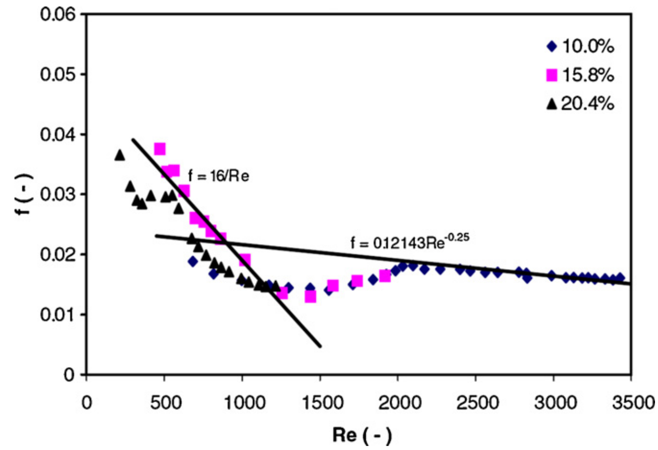


Fig. 9. Friction factors vs. Reynolds number [55].

water, for which this concentration resulted to be a good compromise between storage capacity and pressure drop. Chen et al. [30] observed that pumping power decreased considerably in comparison to water due to the higher transported heat. The decrease could be of up to 67.5%. Zhang and Zhao [32] investigated the rheological properties of two mPCM slurries. Overall these mPCM slurries could be considered as Newtonian fluids when the shear rate is higher than 200 s^{-1} and PCM microcapsules concentration lower than 35%. The viscosity was higher for slurries with bigger PCM microcapsules.

Table 4 shows the viscosity values of different PCM slurries studied in literature.

All consulted studies coincide when remarking that even with PCM concentrations close to 20–30%, the pressure drop of mPCM slurries and emulsions is slightly superior to water, and practically the same in turbulent regime.

4.4. Thermal properties: Thermal conductivity

One of the main disadvantages of thermal energy storage systems with PCMs is their low thermal conductivity. This circumstance results in slow charging and discharging. In the bibliography, there are numerous studies aimed at the improvement of the thermal conductivity of the PCM, either by embedding structures of materials with high thermal conductivity, or by using finned heat exchangers or encapsulating the PCM in containers with a high surface/volume ratio. This is the reason why PCM microcapsules are interesting. Due to the microscopic size of the PCM microcapsules or droplets, the PCM slurry can be treated as a homogeneous material. This assumption implies in that the temperature gradients inside the solid are negligible. This is accomplished if the convective thermal resistance inside the microcapsules is low in comparison to the convective thermal resistance between the microcapsule and its surroundings. The fulfilment of this condition can be analyzed through the Biot number, which should be under 0.1. If the Biot number is calculated for a PCM microcapsule, a value much lower than 0.1 will be obtained. This means that there is no conduction inside the microcapsule and therefore temperature gradients can be neglected. When the PCM is microencapsulated, low thermal conductivity ceases to be a problem [58].

So, PCM slurries in water can improve heat transfer as a consequence of the relationship area/volume of droplets in the case of emulsions and of microcapsules in the case of slurries, in comparison to systems in which the PCM is macroencapsulated. Besides, the fact of dispersing phase change particles into a fluid can improve heat transfer through convection with respect to water. These slurries can serve either as thermal storage materials or heat transfer

Table 4
Viscosity values for different PCM emulsions and mPCM slurries studied in literature.

		PCM	Weight concentration	Viscosity	Ref.
Dispersion system	PCM emulsion	Mixture of n-alkanes	50%	25 mPa s (7 °C, stress = 3 Pa)	[5]
		Tetradecane	10% 20% 30%	1.25 mPa s (35 °C) 2.33 mPa s (38 °C) 2.95 mPa s (38 °C)	[14]
		l-Bromohexadecane	5%	2.05 mPa s (10 °C) 1.54 mPa s (20 °C)	[57]
			10%	2.23 mPa s (10 °C) 1.81 mPa s (20 °C)	
			15.80%	4.18 mPa s (10 °C) 3.32 mPa s (20 °C) Newtonian behavior starting at 600 1/s	
	mPCM slurry	Tetradecane	5%	0.98 mPa s (25 °C) 2.74 mPa s (5 °C)	[14]
			10%	1.04 mPa s (25 °C) 1.85 mPa s (5 °C)	
			15%	1.54 mPa s (25 °C) 1.57 mPa s (5 °C)	
			20%	1.94 mPa s (25 °C) 1.39 mPa s (5 °C)	
			25%	3.31 mPa s (25 °C) 5.23 mPa s (5 °C)	
			30%	4.21 mPa s (25 °C) 5.53 mPa s (5 °C)	
			35%	4.11 mPa s (25 °C) 5.84 mPa s (5 °C)	
			40%	12.58 mPa s (25 °C) 20.87 mPa s (5 °C)	
		n-Octadecane	5% 10% 20%	1.27 mPa s 2.3 mPa s 4.9 mPa s	[29]
Water				1.307 mPa s (10 °C) 1.002 mPa s (20 °C) 0.798 mPa s (30 °C)	

fluids. The thermal properties of these slurries are different from those of PCM and the fluid in question, which are essential to evaluate the fluid and the heat transfer characteristics of a system with these slurries. The thermal properties to be discussed are thermal conductivity and convection heat transfer coefficient. The analysis of the different studies regarding the convection heat transfer coefficient is presented in a separate section, due to their extension and importance within this review.

The thermal conductivity of diluted dispersions, λ_d, can be evaluated from Maxwell's relationship:

$$\frac{\lambda_d}{\lambda_f} = \frac{2+(\lambda_p/k_f)+2\cdot c\cdot(\lambda_p/(\lambda_f-1))}{2+(\lambda_p/k_f)-c\cdot(\lambda_p/(\lambda_f-1))} \quad (1)$$

where λ_p is the thermal conductivity of the disperse phase, λ_f is the thermal conductivity of the continuous phase and c is the volumetric concentration of the disperse phase. As a consequence of the interactions particle/fluid, the effective thermal conductivity is greater than that predicted by this equation, and can be obtained from the following correlation:

$$\frac{\lambda_e}{\lambda_f} = 1+B\cdot c\cdot Pe_p^m \quad (2)$$

where Pe_p is the Peclet number for the particle. The values of B and m depend on the Peclet number of the particle. In general, the thermal conductivity of phase change particles is not very elevated and must be improved [59]. Xuan et al. [60] developed a new type of heat transfer fluid, consisting of a magnetic slurry with microencapsulated PCM that incorporated the advantages of microencapsulated PCM and of a magnetic fluid. Iron nanoparticles were added to the melamine–urea–formaldehyde capsule surrounding the paraffin. Thermal conductivity was measured through the hot wire method. The measured data pointed out that among all particle components, the content of iron nanoparticles was the dominating factor on thermal conductivity. The thermal conductivity ratio increased linearly with the increase in concentration of iron nanoparticles inside the capsules. Similarly, Ho and Gao [61] prepared a n-octadecane emulsion with alumina particles. Compared bulk paraffin, the emulsion presented a higher thermal conductivity, depending on the concentration of the alumina particles. This relationship was not linear. Improvements between 2 and 6% were obtained with weight concentrations of alumina between 5 and 10%. Ho et al. [62] managed to improve the thermal conductivity of PCM emulsions by adding alumina nanoparticles, to values even better than those of water. Table 5 shows some thermal conductivity values for studied slurries in literature.

5. Heat transfer

The main objective of the publication by Kasza and Chen [63] was to point out the benefits of the use of PCM slurries in water, such as the improvement in heat transfer and increase in storage efficiency. Some of the specific benefits mentioned were: 1) reduction in the temperature difference between source and drain, 2) increase of the heat capacity of the fluid, as a consequence of the PCM dispersion, giving place to a lower mass flow and therefore a lower pumping consumption, 3) dynamic use of the PCM. In a conventional system, heat exchange between PCM (static use) and a separated heat transfer fluid is needed to transport heat or cooling. Nevertheless with PCM slurries, thermal storage and the heat transfer fluid are integrated into the PCM slurry. The energy losses of the

Table 5
Thermal conductivity values for mPCM slurries studied in literature.

	PCM	Weight concentration	Thermal conductivity (W/(m K))	Ref.
mPCM slurry	n-Octadecane	5% 10% 20%	0.571 (a 20 °C) 0.541 (a 20 °C) 0.483 (at 20 °C)	[29] Calculated with Eq. (1)
	l-Bromohexadecane	5% 10% 15.80% 20.40% 27.60%	0.568 (at 20 °C) 0.539 (at 20 °C) 0.506 (at 20 °C) 0.48 (at 20 °C) 0.446 (at 20 °C)	[55] Calculated with Eq. (1)
	n-Eicosane	5% (with 10% alumina nanoparticles) 10% (with 10% alumina nanoparticles)	0.66 (at 30 °C) 0.62 (at 30 °C)	[62]
Agua			0.60 (a 20 °C) 0.61 (a 30 °C)	

heat exchange will be annulled, as the necessity for a secondary heat transfer fluid is eliminated.

The possible improvement mechanisms for heat transfer are enumerated. Improvement in heat transfer occurs in slurries, with or without phase change. This improvement is substantially greater when considering PCM slurries. Several mechanisms responsible for this improvement were examined, including particle rotation and migration in the flow as well as the role of phase change.

The following sections show a review of the studies carried out up to date on the heat transfer phenomenon (mainly forced convection inside a tube) and were classified in accordance to the type of fluid (mPCM slurry or PCM emulsion), to the character (experimental or numerical), and to flow regime (laminar or turbulent). Boundary conditions and geometry were also accounted for. The following compilation aims at completing the subsection on numerical models of heat transfer phenomenon in mPCM slurries of the review of Dutil et al. [64], on PCM and mathematical models.

5.1. Heat transfer by forced convection in PCM emulsions

5.1.1. Laminar flow. Experimental studies

Roy and Avanic [65] presented the results of an experimental study on heat transfer by convection in a circular tube, through which circulated a n-octadecane emulsion. The experimental results showed that the characteristics of heat transfer by convection in laminar flow for the emulsion were similar to those of microencapsulated PCM slurry. This means that the walls of the microcapsules did not have a significant effect on the heat transfer process. The results also showed that heat transfer as a whole did not change significantly even with very high concentrations. The experiments also verified that the Reynolds number was not an independent parameter for the heat transfer process. From an application viewpoint, subcooling and the melting temperature range must be considered in future works. The type of slurry (PCM emulsion or mPCM slurry) must be selected considering fluid-dynamics criteria and not heat transfer criteria.

5.1.2. Turbulent flow. Experimental studies

Choi et al. [33] investigated the increase of the convective heat transfer coefficient in the case of a hexadecane emulsion in an experimental installation. The local convection heat transfer coefficient improved with respect to water. The study proposed a melting model with three regions: a first region where the average emulsion temperature is below melting temperature, a second region where phase change takes place, and a third region where the PCM is completely melted. The local convective heat transfer coefficient increased in region 1, decreased abruptly in region 2, and increased slightly in region 3. The authors use the hypothesis that region 1 presented a very thin layer of melted particles, which increased rapidly in region 2 preventing the transportation of solid particles to the wall, and in region 3 there were no solid particles. As average temperature increased in the direction of the flow, the viscosity decreased and the Reynolds number increased, giving place to a slight increment in the heat transfer coefficient. It is also speculated that when the heat flux is very high, the layer of melted particles close to the wall becomes thicker, preventing the radial migration of solid particles from the center to the wall, resulting in this way in a lower convection coefficient. Choi and Cho [34] studied experimentally the effect of the ratio height/width of rectangular channels through which circulated a paraffin emulsion ($C_{22}H_{46}$), of its concentration, of the heat flux and of the Reynolds number, on the heat transfer phenomenon. The local heat transfer coefficients were higher for emulsions than for water as a consequence of: 1) rupture of the laminar sublayer by the paraffin particles, 2) direct heat transfer due to the impact particle-wall, and 3) latent heat of paraffin. The influence of the ratio height/width of the channel on the heat transfer coefficients both for water and emulsion were higher with higher heat fluxes.

5.2. Heat transfer by forced convection in mPCM slurries

5.2.1. Laminar flow. Numerical studies

Charunyakorn et al. [59] modeled the heat transfer phenomenon for mPCM slurries circulating through a circular tube under a constant heat flux. The mathematical model was solved using an implicit finite difference method. Heat generation (or absorption) was included in the energy equation as a heat source due to phase change of the particles. The Stefan number and the PCM concentration were the dominating parameters. The effect of modifying the Peclet number was not significant. The effect of the ratio of duct/particle radiuses was weak but perceptible in the range 50–200 and insignificant for a radius range 200–400. The results showed that the slurry could improve the heat transfer coefficient. This improvement could be used as a higher heat transfer rate, a reduction in mass flow, or a more effective control of the wall temperature. Zhang and Faghri [66] presented a numerical solution for the problem of convection heat transfer in mPCM slurry in a circular tube with constant heat flow under laminar flow conditions. The authors pointed out that one of the most important reasons for the differences in heat transfer between previous experimental and theoretical studies could be the non-consideration of subcooling, the microcapsule coating the PCM, and the melting temperature range. Their numerical model considered these factors and in this way, the difference between numerical and experimental results was decreased. The results also showed that heat transfer by forced convection was reduced with an increase in width of the phase change temperature range. Roy and Avanic [67] introduced the specific heat as a function of temperature in the energy equation when

studying the heat transfer phenomenon in mPCM slurries, under laminar regime conditions and constant heat flux. The effects of phase change were incorporated directly in the energy equation, assuming the heat capacity of the phase change material as a function of temperature. The numerical study showed that the Stefan number was the only parameter with a significant impact on heat transfer for the typical mPCM slurries and for typical operation conditions. The subcooling effects could be important at low heat fluxes or when the input temperature was much lower than melting temperature. The melting temperature range had a significant impact when it was wide. A correlation was developed to predict the increment in wall temperature in function of the distance along the length of the tube. Hu and Zhang [68] studied numerically the convection heat transfer of mPCM slurries circulating through a circular tube under constant heat flux. It was concluded that the exact nature of the phase change process affected the improvement degree of heat transfer through convection. The Stefan number and the PCM concentration resulted to be the most influential parameters on the improvement of heat transfer in mPCM slurries. Nevertheless, subcooling, phase change temperature range and particle diameter also influenced the improvement of heat transfer. Heat transfer improved when subcooling and phase change temperature range decreased, and when particle diameter increased. The improvement would be more notable in a tube with smaller diameter and greater in the completely developed region than in the entry region. Lu and Bai [69] presented a numerical model to analyze heat transfer by convection in mPCM slurries under laminar flow. When the microcapsule radius increased, the heat transfer efficiency increased. The increase in the volumetric fraction of the PCM particles could result in an improvement of heat transfer for a constant heat flux. When the Stefan numbers increased, the heat transfer efficiency was lower. Heat transfer also improved when the Reynolds number was increased. Xing et al. [70] carried out a parametric study from a numerical model for mPCM slurries in microchannels. From this study it was concluded that for a given Reynolds number and PCM concentration, there was an optimum heat flux through the wall that resulted in a maximum effectivity factor (ratio between the heat absorbed by the mPCM slurry and the heat absorbed by water). Also for a given Reynolds number and PCM concentration, there was a maximum index for the optimal heat flux; where this index compared the ratio between the absorbed heat and pumping work of the slurry against water. When the Reynolds number increased, the maximal effectivity factor decreased. In general, the increase in Reynolds resulted in a decrease of the ratio heat absorbed/pumping power. The model also determined that the results were very sensible to the inlet temperature of the fluid in the test tube, which could explain the discrepancies with the experimental results of literature. The convection heat transfer coefficient reached a peak at the moment of phase change. In the region before and after melting, the heat transfer coefficients were lower than water. Fig. 10 shows the local heat transfer coefficient for the slurry for different Reynolds numbers for a given heat flux. Zhao et al. [71] presented the results of simulations to evaluate the convective heat transfer for mPCM slurries, circulating through a circular tube with the boundary condition of constant wall temperature. The most influential parameters on the improvement of heat transfer were the Stefan number, the volumetric concentration, and the ratio particle/tube radiuses. Heat transfer improved when the Stefan number decreased, when volumetric concentration increased or when the ratio particle/tube radiuses increased. The influence of particle diameter on the improvement of heat transfer originated from the microconvection caused by the microcapsules in suspension, instead of the high heat capacity due to phase change. The Reynolds number was the most dominating parameter on the length of the phase change region. The authors remark that it is difficult to develop a simple and general correlation due to the complexity of the combined effects. Sabbah et al. [72] used Fluent to solve the heat transfer phenomena in rectangular microchannels (width 100 μm, height 500 μm and length 10 mm), through which circulated a mPCM slurry in laminar flow under constant heat flux conditions. The use of low concentrations of PCM gave place to a better cooling than the case of water for high heat flux. The improvement index was greater for lower concentrations due to the elevated increase in the viscosity of slurry along with concentration. The use of the mPCM slurry against water only reduced the temperature of the heat dissipated. Increasing the velocity of the slurry increased the heat transfer coefficient, always when the PCM melted inside the channel. In order to achieve a high improvement index for a given heat flux, the cooling system must be designed so that the PCM particles start melting at the entrance of the channel and, when leaving, are completely melted. The use of the slurry properties dependent on temperature was crucial. Zeng et al. [57] adopted both experimental and numerical methods in their study, to analyze the convective heat transfer coefficient in microencapsulated l-bromohexadecane slurries in a circular tube under constant heat flux conditions. This work considered the heat capacity as a sine function of temperature. The investigation focused on the completely developed thermal region to avoid the influence of thermal development. Three types of fluid were studied: pure water, water with microcapsules without phase change, and mPCM slurry, to separate the influence of phase change and microcapsules. The Nusselt number and the dimensionless wall temperature were utilized to study heat transfer. The addition of microcapsules without phase change improved effective thermal conductivity. This improvement of the thermal conductivity resulted in an improvement of the local Nusselt number. With the PCM microcapsules, the Nusselt number tended to draw a wave in the phase change region, as can be observed in Fig. 11. However, the average Nusselt number did not change very much. During phase change, the authors attribute the decrease in wall temperature mainly to the contribution of the variable Cp, and not to the improvement in the heat transfer index between flow and wall. The amplitude of fluctuation of the Nusselt number increased with the decrease in phase change temperature range. This fluctuation also increased when the Stefan number decreased during phase change. The Nusselt number increased when the PCM concentration also increased, along with increases of the Reynolds number and the microcapsule diameter. Kuravi et al. [73] developed a 3D model to simulate the heat transfer phenomenon in a nanoencapsulated octadecane slurry in a poly alpha olefin-based oil (dielectric oil use in cooling) circulating through microchannels (width 200 μm, height 50 μm and length 250 μm) in laminar regime and under boundary conditions of

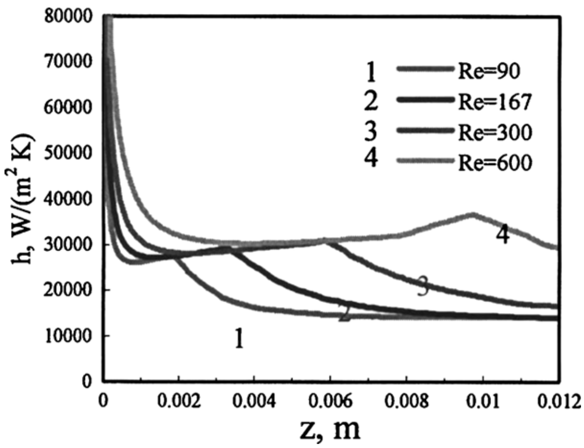


Fig. 10. Heat transfer coefficients for different Reynolds numbers [70].

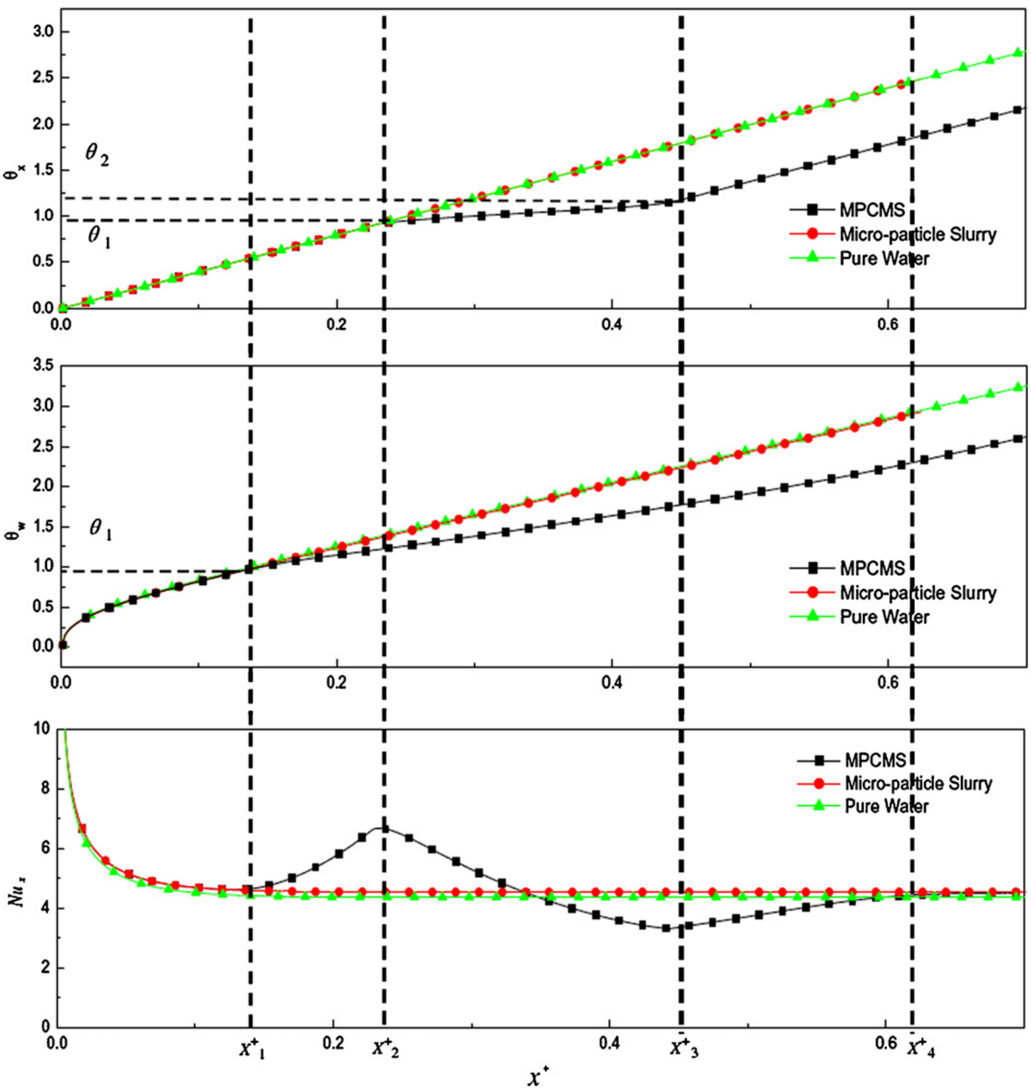


Fig. 11. Calculated Nu and temperature profile of the wall and PCM suspension [57].

constant heat flux. A sine function was used to model phase change. The results showed an increase of the Nusselt number with an increase of PCM concentration, which decreased with the increase in heat flux. For the considered mass flows, an increment in heat flux resulted in an improvement of the heat transfer phenomenon. The authors comment that, based on their numerical results, if the melting temperature range is narrow, the temperature at the microchannel entry should be close to the peak temperature of the PCM melting curve. These results depended on the dimensions of the channel.

5.2.2. *Laminar flow. Experimental studies*

Goel et al. [74] carried out an experimental study utilizing a microencapsulated n-eicosane slurry to evaluate heat transfer under laminar flow conditions in a circular tube with constant heat flux. It was concluded that the Stefan number was the dominating parameter in heat transfer. The volumetric concentration did not have a significant direct effect on heat transfer. Nevertheless, concentration is included in the definition of the Stefan number and therefore has an indirect effect. A higher ratio between the diameters microcapsule/tube improved heat transfer. It was also proved that the homogeneity degree of the slurry could be neglected, but required a deeper experimental investigation. The results adjusted well qualitatively with the work of Charunyakorn et al. [59], but the quantitative adjust was not good. The results showed that a decrease of 50% could be achieved in the temperature wall using microcapsules. The best results were achieved utilizing lower Stefan numbers (Ste < 1), i.e., either with a PCM with a high latent heat, or increasing concentration, or reducing the diameter of the tube. The authors also remarked that another important parameter was the inlet temperature or initial subcooling. For inlet temperatures lower than melting temperature, the reduction in temperature due to energy storage was eclipsed by the sensible heat process until melting temperature is reached. Rao et al. [29] compared experimentally the results obtained using water and microencapsulated n-octadecane slurries with weight concentration from 5 to 20%, under the same thermal conditions and mass flows, when circulating through rectangular microchannels (hydraulic diameter 2.71 μm) under laminar regime. The mPCM slurry showed a better cooling behavior compared to water for low mass flows. The reduction in the wall temperature was higher when the concentration of microencapsulated PCM increased, and the heat transfer coefficient and Nusselt number increased with concentration. When the mass flow was increased, the cooling of the mPCM slurry was less effective. For each slurry, the heat transfer coefficient and the Nusselt number increased along with the increase of mass flow, but this increase was less noticeable when the PCM concentration increased. Heat transfer at higher concentrations was

less effective in high mass flows due to a lower residence time in the channels, lower thermal conductivity and less active movement of the slurry particles. The experiments of Wang et al. [55] to study heat transfer in a circular tube covered both the case of laminar flow and slightly turbulent flow for a microencapsulated l-bromohexadecane slurry under constant heat flux. The local heat transfer coefficients obtained for the mPCM slurry were higher than water. The authors attribute this improvement to the latent heat associated with phase change. In the case of laminar flow, these local heat transfer coefficients increased with the fraction of PCM in the fluid. In the case of turbulent flow, the local heat transfer coefficients were significantly influenced by the heat flux through the test section, and the maximum values of the heat transfer coefficients occurred before for a higher heat flux. Heat transfer was considerably influenced by the turbulence degree of the flow. A correlation for laminar regime was proposed, which predicted satisfactorily the local heat transfer coefficient with a 15% error.

5.2.3. Turbulent flow. Numerical studies

Roy and Avanic [75] modeled heat transfer under turbulent flow conditions in a circular tube with constant heat flux, as previous publications only presented numerical models considering laminar flow conditions while most engineering applications involve turbulent flows. In the proposed method, the effects of phase change are directly incorporated in the energy equation, assuming heat capacity as a function of temperature. The most influential parameter in heat transfer was found to be the Stefan number. A considerable reduction in wall temperature was observed for low and moderate values of the Stefan number. The melting temperature range and the subcooling degree were also influential parameters. Royon and Guiffant [6] described a model to study heat transfer in a circular tube for a slurry with millimetric PCM particles, under constant wall temperature conditions. The model is useful to optimize the size of a heat exchanger and allows for the definition of the minimum length of the heat exchanger to store a specific amount of latent energy from the particles. An increase in the mass fraction of particles increased the minimum length from a linear relationship. The effect of the Reynolds number on the minimum length of the heat exchanger was small. A correlation was proposed from the numerical results to determine the characteristics of the exchanger for a PCM slurry.

5.2.4. Turbulent flow. Experimental studies

Alvarado et al. [28] also presented experimental results on the convective coefficient in a circular tube under constant heat flux in turbulent regime. The heat transfer experiments showed that the improvement in heat capacity was considerable even at low mass fractions. The heat transfer coefficient, however, was lower for the case of slurry than for the case of water at the same velocity. An improvement in the thermal conductivity of the slurry could improve heat transfer. The heat transfer coefficient increased considerably during the phase change process. Fig. 12 shows the heat transfer coefficients for a slurry with 7% PCM weight concentration.

Table 6 shows a summary of the studies carried out on the heat transfer phenomena by internal convection in these slurry systems, according to the slurry flow regime, the type of study, geometry and boundary conditions.

5.3. Heat transfer through natural convection in mPCM slurries

Heinz and Streicher [56] studied experimentally a 200-liter tank with a mPCM slurry developed by BASF with a melting temperature of 60 °C, with a typical spiral exchanger, inside which water circulated. As the limiting factor for heat transfer is the natural convection of the surface of the exchanger to the storage fluid, it resulted interesting to study the heat transfer coefficient by natural convection. The heat transfer coefficients decreased as phase change process takes place, due to the reduction in the difference of temperatures between the exchanger and the storage fluid. Due to higher viscosities, the heat transfer coefficient through natural convection decreased when the PCM concentration increased in water. Even with the lowest PCM concentration, 20%, the values of the heat transfer coefficients for natural convection were lower than for water. A very similar study was carried out by Diaconu et al. [78]. An experimental study was carried out on the heat transfer phenomenon of natural convection in a tank filled with a microencapsulated RT6 slurry (organic PCM from the manufacturer Rubitherm), where the heat exchanger through which water circulated consisted of a helicoidal copper tube, used as storage tank for solar air conditioning applications. During phase change of PCM, it was observed that the natural convective coefficient could be up to five times that of water, depending on the temperature conditions. The reason for this improvement could not be justified, as the phase change temperature range overlapped the temperature range in which water presented a drop in the natural convection coefficient. Huang et al. [79] also studied a heat storage system with a helical coil heat exchanger using a mPCM slurry with a phase change temperature 65 °C (produced by BASF) with a 25, 35 and 50% of volumetric concentration of PCM. The mPCM slurry was used as thermal energy storage material and water as secondary heat transfer fluid. The results showed that the mPCM slurry with a volumetric concentration of 50% was not suitable, since the low thermal conductivity and high viscosity reduced the heat transfer from the heat exchanger to the storage media.

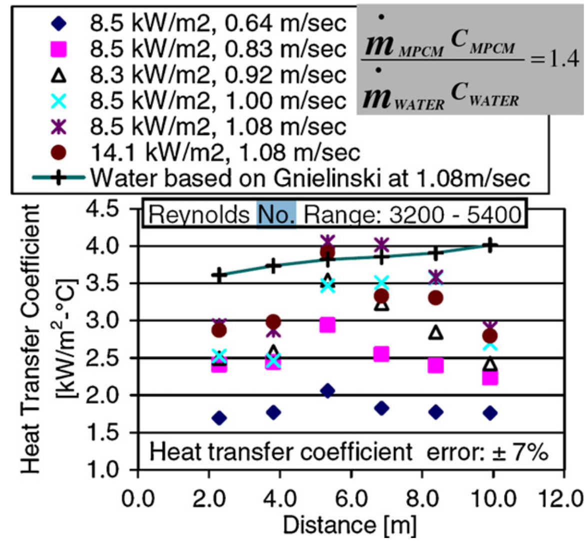


Fig. 12. Heat transfer coefficient for a suspension with 7% PCM [28].

5.4. Other studies

Heinz and Streicher [56], besides studying the phenomenon of convection in a tank filled with a slurry, also studied the heat transfer water-mPCM slurry in a plate heat exchanger. It was observed that the convective heat transfer coefficient decreased with the concentration of PCM, due to a greater viscosity and lower thermal conductivity. With a 20% concentration it decreased 30% in comparison to water, and with a 40% concentration, a decrease of 40% was observed. In spite of the lower overall heat transfer coefficient, the exchanged power of the plate heat exchanger is approximately the same as that of water. This is due to the higher difference in average temperatures, as result of the higher heat capacity of the slurry. The majority of the works, both experimental

Table 6
Compilation of studies carried out on the heat transfer phenomenon in PCM emulsions and mPCM slurries.

	Flow regime	Type of study	Boundary condition	Geometry	Simulation tool/Numerical formulation	Experimental validation?	Ref.
PCM emulsions	Laminar	Experimental	Constant heat flux	Circular tube	–	–	[65]
	Turbulent		Constant heat flux	Circular tube	–	–	[33]
			Constant heat flux	Rectangular channels	–	–	[34]
mPCM slurries	Laminar	Numerical	Constant heat flux	Circular tube	Finite differences. 2D	Ahuja [76]. Experimental validation without phase change. Differences not quantified.	[59]
			Constant heat flux	Circular tube	Finite differences. 2D	Goel et al. [74]. Differences of 34%.	[66]
			Constant heat flux	Circular tube	Fortran 90. Finite differences. 1D	Roy and Avanic [67]. Very small differences.	[67]
			Constant heat flux	Circular tube	Finite differences. 2D	Goel et al. [74]. Differences under 6%.	[68]
			Constant heat flux	Circular tube	Finite differences. 2D	Goel et al. [74]. Numerical results adjusted well to experimental results.	[69]
			Constant heat flux	Circular tube	Finite differences. 2D	Goel et al. [74]. Good adjust between experimental and numerical results, and sensible to entry temperature.	[70]
			Constant wall temp	Circular tube	Finite differences. 2D	No. All available experimental results were limited to constant heat flux conditions.	[71]
			Constant heat flux	Rectangular channels	Fluent 6.2. 3D	Goel et al. [74]. Adapted the geometry of their model. The numerical results adapted well to the experimental results.	[72]
			Constant heat flux	Circular tube	Finite differences. 2D	Zeng et al. [57]. Differences under 9.4%.	[57]
			Constant heat flux	Rectangular channels	Comsol. Finite elements. 3D	Goel et al. [74]. Adapted the geometry of their model. The numerical results adapted well to the experimental results.	[73]
		Experimental	Constant heat flux	Circular tube	–	–	[74]
			Constant heat flux	Rectangular channels	–	–	[29]
			Constant heat flux	Circular tube	–	–	[55]
	Turbulent	Numerical	Constant heat flux	Circular tube	Finite differences. 2D	Choi [77]. Differences around 10–20%.	[75]
			Constant wall temp	Circular tube	Mathematica. Finite differences. 1D	Validation with analytical solution without phase change.	[6]
		Experimental	Constant heat flux	Circular tube	–	–	[28]

and numerical, have assumed that the dispersed PCM and water are in thermal equilibrium. Nevertheless, Diaconu [80] analyzed through simulation the heat transfer phenomenon between the PCM microcapsules and water. The results considered a convective coefficient between microcapsules and water, and it was observed that the temperatures of water and PCM microcapsules were very close, which was attributed to the great exchange area between the PCM microcapsules and water. The greater differences between the temperatures of water and PCM microcapsules occurred during melting/solidification. Inaba et al. [81] developed a numerical two-dimensional model to study natural convection in a rectangular building with a non-Newtonian slurry of mPCM. The heat transfer coefficients were higher when compared to slurries without phase change. When the PCM concentration increased within the range 20–40%, the convection coefficient decreased, while for the range 10–20%, the convective coefficient improved.

6. Applications

For the moment, the main application present in literature is the utilization of these PCM emulsions and mPCM slurries as thermal storage materials and heat transfer fluids in chilled ceilings. Wang and Niu [82] presented the results of a mathematical simulation of a combined system of chilled ceiling and storage tank with a mPCM slurry, in addition to an air treatment unit for the ventilation necessities, in a room with the climatology of Hong Kong. The slurry was cooled and stored in the tank during the night, which resulted in electricity peak shaving, taking advantage of the nocturnal tariff and of a higher COP of the machine due to operation during lower environmental temperatures. During working hours, the mPCM slurry flowed from the tank to the chilled ceiling, melting the PCM and releasing the latent heat. The combination of the chilled ceiling plus storage tank against a conventional water system achieved peak shaving, and therefore a smaller cooling unit/chiller could be sufficient. Three systems were compared regarding energy consumption: 1) Conventional system without storage, 2) Nocturnal storage with mPCM slurry, 3) Storage with ice, where the loads of the air treatment unit and chilled ceiling were supplied by the tank. The consumptions were practically the same for the mPCM slurry and water. Nevertheless, it must be taken into account that calculations were carried out using the same COP for the case of the tank with water and mPCM slurry, when in reality the COP for the case of the tank with mPCM slurry is higher due to operation at lower environment temperatures (charging during the night). The electrical power will be lower. For ratios up to 2.4 (diurnal tariff/nocturnal tariff), the tank with mPCM slurrry presents higher economic benefits. Griffiths and Eames [45] studied experimentally the pumping of a mPCM slurry from BASF manufacturer through a chilled ceiling in a room. The room was tested during four months with a 40% PCM concentration. When water was pumped through the chilled ceiling, a mass flow of 0.7 l/s was required for an inlet temperature of 16 °C and outlet temperature of 18 °C, maintaining the room at 19 °C. When water was substituted by the mPCM slurry, the slurry was capable of maintaining a temperature of 20–21 °C with a mass flow of 0.25 l/s. This means that the ceiling required a lower mass flow (pumping savings were not quantified), could absorb energy at a constant temperature, avoiding increments in the panel surface temperature when internal gains increased.

Another well known application, similar to the previously described, was carried out at the Narita Airport in Tokio by Shibutani [83]. The issue in the installation of the Narita Airport in Tokio was the change of refrigerants due to environmental reasons. When R11 and R22 were substituted by R134a and R123 without changing the chiller unit, this resulted in lower cooling power and the chiller was non-capable to absorb the demand peaks at specific times of the day. This problem was solved through the installation of a tank filled with a mPCM slurry custom-developed by Mitsubishi Heavy Industries. The characteristic temperatures on the demand side were a supply temperature of 5 °C and a return flow temperature of 12 °C. A mPCM slurry was selected with a phase change

Table 7
Objective magnitudes and influential parameters at the time of selection of a PCM emulsion or mPCM slurry as heat transfer fluid or thermal storage material.

Influential factors or parameters	Objective magnitudes	Influence when the factor increases	
		Positive influence	Negative influence
Particle diameter	Rupture of microcapsules		Rupture pressure of microcapsules decreases, higher number of ruptured capsules.
	Subcooling	Greater probability of existing nucleation agents, and therefore lower subcooling.	
	Apparent hysteresis		Possible non-equilibrium between PCM and water temperatures, possibility of hysteresis
	Heat transfer	Improvement in convection coefficient.	
PCM concentration	Stability of emulsions		Creaming speed increases
	Heat capacity	Increase in heat capacity, increase in transported heat.	
	Pressure drop		Increase of viscosity, increase of pressure loss and pumping work. Up to PCM concentrations of 15–20% the increase is slightly superior to water.
	Heat transfer	Decrease in Stefan number and therefore improvement of convection coefficient.	Increase in viscosity, decrease in turbulence degree, and therefore worsening or convection coefficient.
Operation temperature range	Heat transfer	The operation temperature range must fit with the phase change temperature range, and be the narrowest possible.	Decrease of thermal conductivity, occasioning deterioration in heat transfer.

temperature range between 5 and 8 °C. The demand peaks occurred between 8:00 and 22:00, and therefore the cooling produced during the night by the chiller unit could be stored and reduce the demand peaks during the day. The slurry presented a storage density of 67 MJ/m^3, lower in comparison to an ice tank, 167 MJ/m^3, but higher in comparison to water, 21 MJ/m^3. Both the COP of the system and the operational costs for water and mPCM slurry were similar and lower than the ice tank.

Pollerberg and Dötsch [51] proposed an emulsion with a 20% weight concentration of tetradecane (melting temperature = 5 °C) for cooling supply networks. In this way, the required volumetric flow was low, allowing for the reduction of the pumping power and pipe dimensions, with lower operation and investment costs. The results compared three scenarios for a fictitious cooling supply network: tetradecane emulsion, ice slurry and water. The calculations considered the generation and distribution costs of cooling. A power of 500 kW was assumed, with a distribution length of 600 m and 1000 operation hours throughout the year.

As a consequence of the higher heat capacity of the ice slurry, these presented lower distribution costs. The distributions costs for the emulsion were lower than those of water. The calculation of distribution costs takes into account the rheological behavior at the time of calculating the pressure drop. Due to the fact that the temperature of the evaporator must be lower in order to produce ice slurries or solidify the tetradecane, the COP of the chiller was worse and therefore the generation of cooling was more expensive. The tetradecane emulsion balanced out the additional generation costs with the reduction in distribution costs, resulting in the lowest specific cost for the three studied cases.

7. Conclusions

From this review it cannot be concluded whether PCM emulsions and mPCM slurries improved the heat transfer phenomenon in comparison to water as a heat transfer fluid, as it depends on the combination of influential factors. The influence direction of these factors is known, but the degree of influence is still unknown. There is a lack of experimental studies, which are required to deepen the analysis carried out herein as well as to validate the results of different numerical studies, as a great part of the studies has been verified through the same reference or with results that did not consider phase change.

After analysis of the works compiled herein, Table 7 summarizes the objective magnitudes at the time of selecting a PCM emulsion or a mPCM slurry as heat transfer fluid or thermal storage material. The table includes the factors that influence the objective magnitudes and how this influence occurs.

This review has focused, on one hand, on the elaboration and fabrication of these new liquids, and on the compilation of the PCM slurries elaborated and utilized up to date in literature. On the other hand, this review focused on the analysis of properties, which is a key factor in the optimal development of storage fluids. The main problems in thermal storage material applications are subcooling and instability issues. In heat transfer fluid applications, it is interesting to achieve a higher heat transfer in comparison to a typical heat transfer fluid, such as water. Nevertheless, after systematic reviews, a clear conclusion still cannot be drawn, as several factors play a role.

For the moment there are very few installation examples that make use of PCM emulsions and mPCM slurries. The main application seems to be oriented towards storage tanks combined with chilled ceilings, shifting the cooling production to the night in order to shave the demand peaks, improve COP, and make better use of nocturnal tariffs. There is also a study on the use of these new fluids in supply networks.

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Web references

http://www.rubitherm.com/ [accessed May 2011].
http://www.micronal.de/portal/load/fid443847/BASF_Micronal_PCM_Brochure%202009_English.pdf [accessed May 2011].
http://www.capzo.nl/index.asp?CategorieID=2&Taal=EN [accessed May 2011].
http://www.microteklabs.com/micropcm_products.html [accessed May 2011].

References

[1] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. Appl Therm Eng 2003;23:251–83.
[2] Inaba H. New challenge in advanced thermal energy transportation using functionally thermal fluids. Int J Therm Sci 2000;39:991–1003.
[3] Mehling H, Cabeza LF. Heat and cold storage with PCM, an up to date introduction into basics and applications. In: Heat and Mass Transfer. Springer; 2008.
[4] Zhang P, Ma ZW, Wang RZ. An overview of phase change material slurries: MPCS and CHS. Renew Sustain Energy Rev 2010;14:598–614.
[5] Royon L, Perrot P, Guiffant G, Fraoua S. Physical properties and thermorheological behaviour of a dispersion having cold latent heat-storage material. Energy Convers Manage 1998;39:1529–35.
[6] Royon L, Guiffant G. Forced convection heat transfer with slurry of phase change material in circular ducts: A phenomenological approach. Energy Convers Manage 2008;49:928–32.
[7] Bédécarrats JP, Strub F, Falcon B, Dumas JP. Phase-change thermal energy storage using spherical capsules: performance of a test plant. Int J Refrig 1996;19:187–96.
[8] Cho K, Choi SH. Thermal characteristics of paraffin in a spherical capsule during freezing and melting processes. Int J Heat Mass Transfer 2000;43:3183–96.
[9] Chen S, Chen C, Tin C, Lee T, Ke M. An experimental investigation of cold storage in an encapsulated thermal storage tank. Exp Therm Fluid Sci 2000;23:133–44.
[10] Huang L, Petermann M, Doetsch C. Evaluation of paraffin/water emulsion as a phase change slurry for cooling applications. Energy 2009;34:1145–55.
[11] Schalbart P, Kawaji M, Fumoto K. Formation of tetradecane nanoemulsion by low-energy emulsification methods. Int J Refrig 2010;33:1612–24.
[12] Monllor Pérez P. Caracterización de microencapsulados aplicados sobre materiales textiles; 2007.
[13] Su J, Huang Z, Ren L. High compact melamine-formaldehyde microPCMs containing n-octadecane fabricated by a two-step coacervation method. Colloid Polym Sci 2007;285:1581–91.
[14] Yang R, Xu H, Zhang Y. Preparation, physical property and thermal physical property of phase change microcapsule slurry and phase change emulsion. Sol Energy Mater Sol Cells 2003;80:405–16.
[15] Schmidt M. Phase Change Materials—latent heat storage for interior climate control. BASF Micronal, Energiforum Danmark; 2008.
[16] Su J, Ren L, Wang L. Preparation and mechanical properties of thermal energy storage microcapsules. Colloid Polym Sci 2005;284:224–8.
[17] Fan YF, Zhang XX, Wu SZ, Wang XC. Thermal stability and permeability of microencapsulated n-octadecane and cyclohexane. Thermochim Acta 2005;429:25–9.
[18] Su J, Wang L, Ren L. Synthesis of polyurethane microPCMs containing n-octadecane by interfacial polycondensation: Influence of styrene-maleic anhydride as a surfactant. Colloids Surf A: Physicochem Eng Aspects 2007;299:268–75.
[19] Zhang X, Fan Y, Tao X, Yick K. Crystallization and prevention of supercooling of microencapsulated n-alkanes. J Colloid Interface Sci 2005;281:299–306.
[20] Zhang X, Xiao-Ming T, Kit-Lun Y, Xue-Chen W. Structure and thermal stability of microencapsulated phase-change materials. Colloid Polym Sci 2004;282:330–6.
[21] Jin Z, Wang Y, Liu J, Yang Z. Synthesis and properties of paraffin capsules as phase change materials. Polymer 2008;49:2903–10.

[22] Alkan C, Sarı A, Karaipekli A, Uzun O. Preparation, characterization, and thermal properties of microencapsulated phase change material for thermal energy storage. Sol Energy Mater Sol Cells 2009;93:143–7.
[23] Fang Y, Kuang S, Gao X, Zhang Z. Preparation and characterization of novel nanoencapsulated phase change materials. Energy Convers Manage 2008;49:3704–7.
[24] Zhang XX, Fan YF, Tao XM, Yick KL. Fabrication and properties of microcapsules and nanocapsules containing n-octadecane. Mater Chem Phys 2004;88:300–7.
[25] Sarı A, Alkan C, Karaipekli A, Uzun O. Microencapsulated n-octacosane as phase change material for thermal energy storage. Sol Energy 2009;83:1757–63.
[26] Hawlader MNA, Uddin MS, Khin MM. Microencapsulated PCM thermal-energy storage system. Appl Energy 2003;74:195–202.
[27] Li W, Zhang X, Wang X, Niu J. Preparation and characterization of microencapsulated phase change material with low remnant formaldehyde content. Mater Chem Phys 2007;106:437–42.
[28] Alvarado JL, Marsh C, Sohn C, Phetteplace G, Newell T. Thermal performance of microencapsulated phase change material slurry in turbulent flow under constant heat flux. Int J Heat Mass Transfer 2007;50:1938–52.
[29] Rao Y, Dammel F, Stephan P, Lin G. Convective heat transfer characteristics of microencapsulated phase change material suspensions in minichannels. Heat Mass Transfer 2007;44:175–86.
[30] Chen B, Wang X, Zeng R, Zhang Y, Wang X, Niu J, et al. An experimental study of convective heat transfer with microencapsulated phase change material suspension: laminar flow in a circular tube under constant heat flux. Exp Therm Fluid Sci 2008;32:1638–46.
[31] Diaconu BM, Varga S, Oliveira AC. Experimental assessment of heat storage properties and heat transfer characteristics of a phase change material slurry for air conditioning applications. Appl Energy 2010;87:620–8.
[32] Zhang GH, Zhao CY. Thermal and rheological properties of microencapsulated phase change materials. Renew Energy 2011;36:2959–66.
[33] Choi E, Cho YI, Lorsch HG. Forced convection heat transfer with phase-change-material slurries: turbulent flow in a circular tube. Int J Heat Mass Transfer 1994;37:207–15.
[34] Choi M, Cho K. Effect of the aspect ratio of rectangular channels on the heat transfer and hydrodynamics of paraffin slurry flow. Int J Heat Mass Transfer 2001;44:55–61.
[35] Lorsch HG, Murali K, Cho YI. Improving thermal and flow properties of chilled water-Part 1: Material Selection and Instrument Calibration. ASHRAE Trans 1997;103:188–97.
[36] Huang L, Doetsch C, Pollerberg C. Low temperature paraffin phase change emulsions. Int J Refrig 2010;33:1583–9.
[37] Günther E, Schmid T, Mehling H, Hiebler S, Huang L. Subcooling in hexadecane emulsions. Int J Refrig 2010;33:1605–11.
[38] Huang L, Günther E, Doetsch C, Mehling H. Subcooling in PCM emulsions—Part 1: Experimental. Thermochim Acta 2010;509:93–9.
[39] Zou D, Feng Z, Xiao R, Qin K, Zhang J, Song W, et al. Preparation and flow characteristic of a novel phase change fluid for latent heat transfer. Sol Energy Mater Sol Cells 2010;94:2292–7.
[40] Huang L, Noeres P, Petermann M, Doetsch C. Experimental study on heat capacity of paraffin/water phase change emulsion. Energy Convers Manage 2010;51:1264–9.
[41] Salaün F, Devaux E, Bourbigot S, Rumeau P. Development of a precipitation method intended for the entrapment of hydrated salt. Carbohydr Polym 2008;73:231–40.
[42] Günther E, Huang L, Mehling H, Dötsch C. Subcooling in PCM emulsions – Part 2: Interpretation in terms of nucleation theory. Thermochimica Acta 2011;522:199–204.
[43] Alvarado JL, Marsh C, Sohn C, Vilceus M, Hock V, Phetteplace G, et al. Characterization of supercooling suppression of microencapsulated phase change material by using DSC. J Therm Anal Calorim 2006;86:505–9.
[44] Yamagishi Y, Sugeno T, Ishige T. An evaluation of microencapsulated PCM for use in cold energy transportation medium. Proc Intersoc Energy Convers Eng Conf 1996:2077–83.
[45] Griffiths PW, Eames PC. Performance of chilled ceiling panels using phase change material slurries as the heat transport medium. Appl Therm Eng 2007;27:1756–60.
[46] Tadros T. Application of rheology for assessment and prediction of the long-term physical stability of emulsions. Adv Colloid Interface Sci 2004;108–109:227–58.
[47] Choi E, Cho YI, Lorsch HG. Effects of emulsifier on particle size of a phase change material in a mixture with water. Int Commun Heat Mass Transfer 1991;18:759–66.
[48] Gschwander S, Schossig P, Henning H. Micro-encapsulated paraffin in phase-change slurries. Sol Energy Mater Sol Cells 2005;89:307–15.
[49] Barnes HA. A handbook of elementary rheology, Institute of Non-Newtonian Fluid Mechanics. University of Wales; 2000.
[50] Chen B, Wang X, Zhang Y, Xu H, Yang R. Experimental research on laminar flow performance of phase change emulsion. Appl Therm Eng 2006;26:1238–45.
[51] Pollerberg C, Dötsch C. Phase Changing Slurries in cooling and cold supply networks. In: 10th International Symposium on District Heating and Cooling. 2006.
[52] Cho YI, Choi I, Lorsch HG. A novel concept for heat transfer fluids used in district cooling systems, Progress Report. Development of advanced low-temperature heat transfer fluids for district heating and cooling. The U.S. Department of Energy; 1991.
[53] Lorsch HG, Murali K, Chandratre K, Cho YI. Improving thermal and flow properties of chilled water-Part 2: Facility construction and flow tests. ASHRAE Trans 1997;103:198–212.
[54] Rao Y, Dammel F, Stephan P, Lin G. Flow frictional characteristics of microencapsulated phase change material suspensions flowing through rectangular minichannels. Sci China 2006;49:445–56.
[55] Wang X, Niu J, Li Y, Wang X, Chen B, Zeng R, et al. Flow and heat transfer behaviors of phase change material slurries in a horizontal circular tube. Int J Heat Mass Transfer 2007;50:2480–91.
[56] Heinz A, Streicher W. Application of phase change materials and PCM-slurries for thermal energy storage. In: 10th International Conference on Thermal Energy Storage. 2006.
[57] Zeng R, Wang X, Chen B, Zhang Y, Niu J, Wang X, et al. Heat transfer characteristics of microencapsulated phase change material slurry in laminar flow under constant heat flux. Appl Energy 2009;86:2661–70.
[58] Streicher W, Cabeza LF, Heinz A. Inventory of phase change materials. A report of IEA solar heating and cooling programme – Task 32 “Advanced storage concepts for solar and low energy buildings” Report C2 of Subtask C; 2005.
[59] Charunyakorn P, Sengupta S, Roy SK. Forced convection heat transfer in microencapsulated phase change material slurries: flow in circular ducts. Int J Heat Mass Transfer 1991;34:819–33.
[60] Xuan Y, Huang Y, Li Q. Experimental investigation on thermal conductivity and specific heat capacity of magnetic microencapsulated phase change material suspension. Chem Phys Lett 2009;479:264–9.
[61] Ho CJ, Gao JY. Preparation and thermophysical properties of nanoparticle-in-paraffin emulsion as phase change material. Int Commun Heat Mass Transfer 2009;36:467–70.
[62] Ho CJ, Huang JB, Tsai PS, Yang YM. Preparation and properties of hybrid water-based suspension of Al_2O_3 nanoparticles and MEPCM particles as functional forced convection fluid. Int Commun Heat Mass Transfer 2010;37:490–4.
[63] Kasza KE, Chen MM. Improvement of the performance of solar energy or waste heat utilization systems by using phase-change slurry as an enhanced heat-transfer storage fluid. J Sol Energy Eng 1985;107:229–36.
[64] Dutil Y, Rousse DR, Salah NB, Lassue S, Zalewski L. A review on phase-change materials: Mathematical modeling and simulations. Renew Sustain Energy Rev 2011;15:112–30.
[65] Roy SK, Avanic BL. Laminar forced convection heat transfer with phase change material emulsions. Int Commun Heat Mass Transfer 1997;24:653–62.
[66] Zhang Y, Faghri A. Analysis of forced convection heat transfer in microencapsulated phase change material suspensions. J Thermophys Heat Transfer 1995;9:727–32.
[67] Roy SK, Avanic BL. Laminar forced convection heat transfer with phase change material suspensions. Int Commun Heat Mass Transfer 2001;28:895–904.
[68] Hu X, Zhang Y. Novel insight and numerical analysis of convective heat transfer enhancement with microencapsulated phase change material slurries: laminar flow in a circular tube with constant heat flux. Int J Heat Mass Transfer 2002;45:3163–72.
[69] Lu W, Bai F. A new model for analyzing laminar forced convective enhanced heat transfer in latent functionally thermal fluid. Chin Sci Bull 2004;49:1457–63.
[70] Xing KQ, Tao YX, Hao YL. Performance evaluation of liquid flow with PCM particles in microchannels. ASME J Heat Transfer 2005;127:931–40.
[71] Zhao Z, Hao R, Shi Y. Parametric analysis of enhanced heat transfer for laminar flow of microencapsulated phase change suspension in a circular tube with constant wall temperature. Heat Transfer Eng 2008;29:97–106.
[72] Sabbah R, Farid MM, Al-Hallaj S. Micro-channel heat sink with slurry of water with micro-encapsulated phase change material: 3D-numerical study. Appl Therm Eng 2009;29:445–54.
[73] Kuravi S, Kota KM, Du J, Chow LC. Numerical Investigation of flow and heat transfer performance of nano-encapsulated phase change material slurry in microchannels. J Heat Transfer: Trans ASME 2009;131:062901.
[74] Goel M, Roy SK, Sengupta S. Laminar forced convection heat transfer in microcapsulated phase change material suspensions. Int J Heat Mass Transfer 1994;37:593–604.
[75] Roy SK, Avanic BL. Turbulent heat transfer with phase change material suspensions. Int J Heat Mass Transfer 2001;44:2277–85.
[76] Ahuja AS. Augmentation of heat transport in laminar-flow of polystyrene suspensions.1. Experiments and results. J Appl Phys 1975;46:3408–16.
[77] Choi E. Forced convection heat transfer with water and phase-change material slurries: turbulent flow in a circular tube. PhD thesis; 1993.
[78] Diaconu BM, Varga S, Oliveira AC. Experimental study of natural convection heat transfer in a microencapsulated phase change material slurry. Energy 2010;35:2688–93.
[79] Huang MJ, Eames PC, McCormack S, Griffiths P, Hewitt NJ. Microencapsulated phase change slurries for thermal energy storage in a residential solar energy system. Renew Energy 2011;36:2932–9.
[80] Diaconu BM. Transient thermal response of a PCS heat storage system. Energy Build 2009;41:212–9.
[81] Inaba H, Zhang Y, Horibe A, Haruki N. Numerical simulation of natural convection of latent heat phase-change-material microcapsulate slurry packed in a horizontal rectangular enclosure heated from below and cooled from above. Heat Mass Transfer 2007;43:459–70.
[82] Wang X, Niu J. Performance of cooled-ceiling operating with MPCM slurry. Energy Convers Manage 2009;50:583–91.
[83] Shibutani S. PCM-micro Capsule Slurry Thermal Storage System for Cooling in Narita Airport. In: Proc. of 3rd Experts meeting and Workshop of IEA Annex 17. 2002.